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ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY. VOLUME 6: ETHYLENE OXIDE MANUFACTURE BY DIRECT OXIDATION OF ETHYLENE

D. E. Field, et al

Air Products and Chemicals, Incorporated

Prepared for:

Environmental Protection Agency

June 1975

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Office of Air and Waste Management
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16. ABSTRACT

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by twelve distinctly different processes has been selected for this type of in-depth study. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c, and d).

This volume covers the manufacture of ethylene oxide by direct oxidation of ethylene. Included is a process and industry description, an engineering description of available emission control systems, the cost of these systems, and the financial impact of emission control on the industry. Also presented are suggested air episode procedures and plant inspection procedures.

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by

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June 1975

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Publication No. EPA-450/3-73-006-f

PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by 12 distinctly different processes has been selected for this type of in-depth study. These processes are considered to be ones which might warrant standards as a result of their impact on air quality. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c and d).

The ten volumes of this series report on carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride (two processes in a single volume), formaldehyde (two processes in two volumes), ethylene oxide (two processes in a single volume) high density polyethylene, polyvinyl chloride and vinyl chloride monomer.

ACKNOWLEDGEMENTS

The study reported in this volume, by its nature, relied on the fullest cooperation of the companies engaged in the production of ethylene oxide. Had their inputs been withheld, or valueless, the study would not have been possible or at least not as extensive as here reported. Hence, Air Products wishes to acknowledge this cooperation by listing the contributing companies.

BASF-Wyandotte Corporation
Dow Chemical Company
Houston Chemical Corporation
Jefferson Chemical Company
Koch Chemical Company
Northern Petrochemical Company
Union Carbide Chemical Company

Additionally, Air Products wishes to acknowledge the cooperation of the member companies of the U. S. Petrochemical Industry and the Manufacturing Chemists Association for their participation in the public review of an early draft of this document. More specifically, the individuals who served on the EPA's Industry Advisory Committee are to be commended for their advice and guidance at these public meetings.

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SUMMARY

The ethylene oxide industry has been studied to determine the extent of air pollution resulting from the various plants and processes of the industry. The purpose of the work was to provide the Environmental Protection Agency with a portion of the basic data required in order to reach a decision on the need to promulgate air emission standards for the industry.

It was concluded that the historical chlorohydrin process has been completely superceded by two general types of direct oxidation processes although some of the old chlorohydrin plants may have been converted to propylene oxide production. There are distinct differences in the two types of oxidation processes in that one process uses air as the source of oxidant, has nitrogen as the major constituent of its vent gas, has a relatively smaller recycle stream and utilizes a mole ratio of ethylene to oxygen in the main reactor feed that is less than one. The other process uses relatively high purity oxygen as the oxidant, has carbon dioxide as the major constituent of its vent gas, has a relatively larger recycle stream and utilizes a mole ratio of ethylene to oxygen in the main reactor feed that is greater than one. There are several minor modifications to these basic processes, depending upon the process licensor or designer. The most significant of these is one process that incorporates the addition of methane into the recycle stream of an oxygen oxidation process to serve as an "inert" at process conditions but to make the vent gas combustible in a boiler house. All known processes use a fixed bed silver catalyst in a tubular reactor with heat removal (steam generation) on the exterior of the tubes.

In general terms, the air emissions from all variations of the direct oxidation process are chiefly hydrocarbons (ethylene, ethylene oxide and traces of ethane from the feed gas). Some plants report traces of NOx or SOx from combustion operations associated either with process drive machinery or pollution control. Some minor particulate emissions have been reported from one scrubber operation but there is no explanation of this fact. No carbon monoxide emissions have been reported even though most of the non-selectivity of the process in an "over-oxidation" of ethylene to carbon dioxide and water. This fact can only be assumed to be the result of the thermodynomics at reactor conditions.

The producers of ethylene oxide that utilize air oxidation processes report a trend toward the incorporation of a catalytic converter on the main process vent. This results in the heating of the vent stream to a sufficiently high temperature to have utility in the gas turbine driver of a process compressor. Considering the fact that some plants presently employ these devices and others do not, an estimate of the current (1973) emission factors for air oxidation plants is 0.0287 lbs./lb. of ethylene oxide produced, of which over 99 percent is hydrocarbons. For oxygen oxidation plants, the estimate of emission factors is 0.0124 lbs./lb. of ethylene oxide produced unless methane is added to the recycle and the vent gas burned. In this latter case, the factor is reduced to 0.0038 lbs./lb. of ethylene oxide produced. In each of the oxygen process estimates, data were received from only one plant and the emissions are 100 percent hydrocarbons. A weighted average of these factors results in an overall emission rate of 0.0206 lbs./lb. of ethylene oxide produced (over 99 percent hydrocarbons). This amounted to nearly 90 million pounds of pollutants emitted to the atmosphere in 1973 and would grow to about 140 million pounds per year by 1985 if the same averages were maintained throughout the growth period.

SUMMARY (continued)

As already indicated, air process plants can reduce their emissions and recover energy by means of existing technology and the trend is toward the installation of these units. One of the oxygen oxidation plants reporting does not have a poliution control device on its process vent even though the stream has been estimated to be readily combustible. This is probably due to two facts, namely (1) the stream is quite small so its energy content is small and (2) the process is a net energy producer so this small increment is not needed. The other oxygen oxidation plant that reported adds methane and burns the entire stream in an off-site boiler, presumably to generate steam for an off-site process. Hence, it can be concluded that oxygen oxidation plants can reduce their emissions by one of several incineration techniques. Whether or not they recover the available energy will be dictated by the economics and process considerations in each instance. Assuming that all present and future plants incinerate their vent gases by one of the techniques discussed, 1985 emissions would be reduced to less than 35 million lbs./year. This is an emission factor of 0.005 lbs./lb. of ethylene oxide produced of which about 98 percent is hydrocarbon and about two percent oxides of nitrogen (due to incineration processes).

Although none of the pollution control devices studied can be shown to provide a net positive return on investment from the value of the energy recovered, neither can any of them be deemed a "financial hardship". For a 200 million lbs./year air oxidation process, it has been estimated that about $250,000 of capital equipment (1973 dollars) would be required to install a catalytic incineration/gas turbine system on both the main process vent and the CO_2 purge vent. The net operating costs of these installations would be about $7,400/year after taking credit for energy recovery. About 66 percent of the present industry utilizes the air oxidation process. Hence, by 1985 the total investment for the industry in 1973 dollars would be less than six million if all plants installed these devices and the current ratios are maintained. No data are available on the cost of boilers on oxygen oxidation plants utilizing methane addition, but the cost must be only incremental. On the other type of oxygen oxidation process (about five percent of the current industry), the capital cost (1973 dollars) of a steam generator is about $40,000 and of an incinerator about $16,000. The net operating costs of these devices has been estimated to be $5,900 and $9,600 per year, respectively. Thus, in the worst case, if all oxygen process plants installed a steam generator, their 1985 total investment would be less than $0.5 million and the total industry investment only slightly over $6 million. In addition, by 1985, the industry could save the equivalent of three billion standard cubic feet of natural gas per year by converting all of their air emissions to utilizable energy.

In summary, the study has concluded that the industry can reduce emissions and conserve fuel without significant financial hardship. Air oxidation process plants can accomplish this by means of the demonstrated technology of a catalytic converter and gas turbine on their main process vent. The addition of this concept to the CO_2 purge vent would further reduce emissions although this latter aspect has not been demonstrated. Oxygen oxidation plants should have little trouble incinerating their main process vent in standard types of units although none were reported in use. Those plants that add methane, by necessity, already provide for the incineration of the off-gas. No need for control on the CO_2 purge vent of oxygen oxidation plant is forseen although a stack sampling program should be used to verify this conclusion.

SUMMARY (continued)

It was also concluded that the major areas indicated for industry research are catalyst improvement and/or inhibitor modification. Both of these programs could lead to higher selectivies which would reduce the volume of CO_2 being emitted thereby simplifying the control techniques. These programs could also lead to higher ethylene conversions thus reducing the amount of ethylene that is emitted. There is little doubt that research of this nature is already in progress in the laboratories of catalyst suppliers and process licensors.

1. Introduction

There are two processes for producing ethylene oxide that have been used commercially. The first, the older of the two, is by reacting ethylene with hypochlorous acid and dechlorinating the resultant chlorohydrin with lime to form calcium chloride and ethylene oxide.

(1) $CH_2 = CH_2 + HOCl \longrightarrow HOCH_2CH_2Cl$

(2) $2\ HOCH_2CH_2Cl + Ca(OH)_2 \longrightarrow 2\ CH_2\text{-}O\text{-}CH_2 + CaCl_2 + H_2O$

This is the chlorohydrin process, but all existing units have either been shut down or converted to production of proplyene oxide.

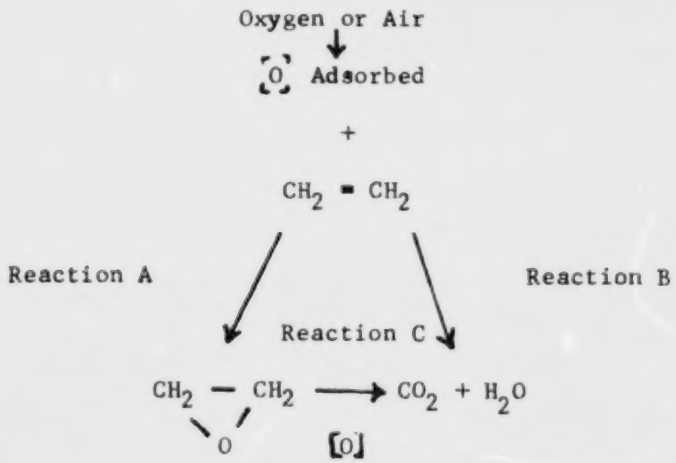
The alternate process for producing ethylene oxide, and the process which currently completely dominates the field, is direct oxidation of ethylene either with air or O_2.

$$CH_2 = CH_2 + \tfrac{1}{2}\ O_2 \xrightarrow{Ag} CH_2\text{-}O\text{-}CH_2$$

Atmospheric emissions from the direct oxidation process are mainly ethylene and related hydrocarbons. Relatively small quantities of SOx (from fuel) and NOx (burners) are reported.

II. Process Description

In the direct oxidation process, oxygen is adsorbed on the surface of a specific, silver containing catalyst. It then adds across the olefinic bond of ethylene. Two routes are possible as shown below:



The course of the reaction, either via route A or route B can be directed by proper control of the temperature at the catalyst reaction sites. A brief description of the thermodynamics involved is presented in Table EO-1.

Flow diagrams for the air and oxygen oxidation process are given in Figures EO-1 and EO-2. The bulk of the respondents use the air oxidation process and as a result, this report will emphasize that process although comparative data for the O_2 process will be given when available. A material balance for a typical air oxidation plant is given in Table EO-2A. This table was compiled from the respondents questionnaires and whatever yield, conversion and selectivity data could be gleaned from the literature. As a result, no one particular plant will actually fit this material balance exactly. It is rather an idealized representation of an ethylene oxide plant which should be close to representing any particular air oxidation plant. Yields in terms of a typical 200 MM Lbs./Year ethylene oxide plant are also shown on Table EO-2A.

Ethylene (95-99% pure) and air are fed separately into a recycle gas stream which then feeds a bank of primary (main) reactors which are operated in parallel. The air/ethylene feed ratio, usually about 10:1, by weight, is varied so that after dilution with recycle gas, an optimum oxygen/ethylene ratio results. Reaction takes place over a silver catalyst packed in tubes in a reactor and surrounded by a heat transfer fluid to control temperature. The gas stream moves downward over the catalyst and counter-current to circulation of the heat transfer fluid in the reactor shell. A portion of the fluid (Dowtherm, tetralin or other high boiling materials) is vaporized by the exothermic reaction heat and is condensed in a heat exchanger to provide considerable steam for the ethylene oxide and other processes. Ethylene conversion in the primary reactors is maintained at about 50 percent per pass in order to insure selectivities of 60 percent or higher. Oxidation inhibitors, such as ethylene dichloride, are added to the inlet gas in PPM concentrations to reduce undesirable CO_2 formation.

TABLE EO-I

HEAT BALANCE

Two main reaction routes are possible when ethylene is oxidized in the presence of a silver containing catalyst.

A. $CH_2 = CH_2 + \frac{1}{2} O_2 \longrightarrow CH_2\text{-}O\text{-}CH_2$ + 1,615 BTU/Lb.* ethylene reacted

B. $CH_2 = CH_2 + 3 O_2 \longrightarrow 2 CO_2 + 2 H_2O$ + 21,790 BUT/Lb.* ethylene reacted

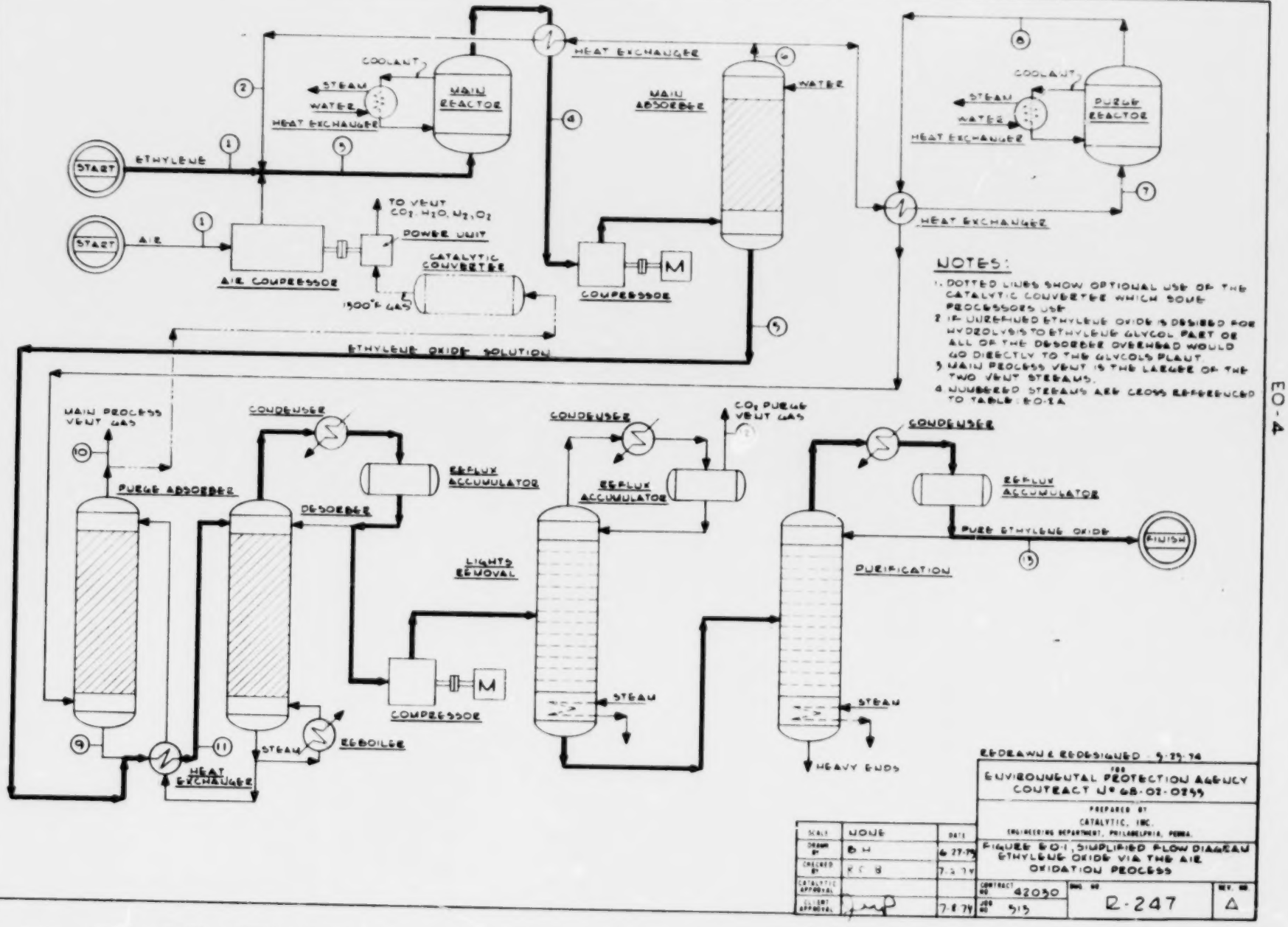
Reaction B liberates over 13 times as much energy as the desired reaction A. Success of a commerical installation depends on the proper control of the temperature on the catalyst surface to favor reaction A.

For example, the effect of temperature on selectivity and heat release has been reported as follows:

Selectivity, %	70	60	50	40
Total Heat Release (1000's BTU/Lb. $C_2^=$ converted)	7.67	9.69	11.70	13.72

A 50 million lb./year ethylene oxide plant would release 40 million BTU/hr. of heat at 70 percent selectivity (optimum). If improper control lowered selectivity to 50 percent, the heat release would more than double to 98 million BTU/hr.

*Gross Heating Value.


START
ETHYLENE
START
AIR
AIR COMPRESSOR
TO VENT
CO_2 H_2O, N_2, O_2
POWER UNIT
CATALYTIC CONVERTER
1500°F GAS
COOLANT
STEAM
WATER
HEAT EXCHANGER
MAIN REACTOR
HEAT EXCHANGER
MAIN ABSORBER
WATER
COMPRESSOR
M
ETHYLENE OXIDE SOLUTION
COOLANT
STEAM
WATER
HEAT EXCHANGER
PURGE REACTOR
HEAT EXCHANGER
NOTES:
1. DOTTED LINES SHOW OPTIONAL USE OF THE CATALYTIC CONVERTER WHICH SOME PROCESSORS USE
2. IF UNREFINED ETHYLENE OXIDE IS DESIRED FOR HYDROLYSIS TO ETHYLENE GLYCOL PART OR ALL OF THE DESORBER OVERHEAD WOULD GO DIRECTLY TO THE GLYCOLS PLANT.
3. MAIN PROCESS VENT IS THE LARGER OF THE TWO VENT STREAMS.
4. NUMBERED STREAMS ARE CROSS REFERENCED TO TABLE 6.0-2A
MAIN PROCESS VENT GAS
CONDENSER
REFLUX ACCUMULATOR
PURGE ABSORBER
DESORBER
CONDENSER
REFLUX ACCUMULATOR
CO_2 PURGE VENT GAS
LIGHTS REMOVAL
CONDENSER
REFLUX ACCUMULATOR
PURE ETHYLENE OXIDE
FINISH
PURIFICATION
COMPRESSOR
M
STEAM
STEAM
STEAM
REBOILER
HEAT EXCHANGER
HEAVY ENDS
REDRAWN REDESIGNED 9-25-74
FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT Nº 68-02-0255
PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA.
FIGURE 6.0-1, SIMPLIFIED FLOW DIAGRAM ETHYLENE OXIDE VIA THE AIR OXIDATION PROCESS
SCALE NONE
DRAWN BY B H 6-27-74
CHECKED BY K C B 7-2-74
CATALYTIC APPROVAL
CLIENT APPROVAL 7-8-74
CONTRACT NO 42030
JOB NO 515
DWG NO R-247
REV NO Δ

6.0-4

TABLE EO-2A
TYPICAL MATERIAL BALANCE (2)
AIR OXIDATION PROCESS
200 MM LBS./YR. (1) ETHYLENE OXIDE

Pounds/Hour (1)	1 Fresh Feed	2 Recycle	3 Gross Reactor Feed	4 Reactor Effluent	5 Absorber Bottoms	6 Absorber Overhead	7 Purge Reactor Feed	8 Purge Reactor Effluent	9 Purge Absorber Bottoms	10 Main Process Vent	11 Recovery Unit Feed	12 CO_2 Purge Vent	13 Ethylene Oxide Product
Nitrogen	124,508	266,603	391,111	391,111	335	390,776	124,173	124,173	49	124,124	384	384	0
Oxygen	37,823	18,954	56,777	27,824	42	27,782	8,828	4,712	6	4,706	48	48	0
Ethane	150	322	472	472	0	472	150	150	0	150	0	0	0
Ethylene	25,342	11,145	36,487	16,419	83	16,336	5,191	2,336	12	2,324	95	95	0
Ethylene Oxide	0	0	0	21,921	21,921	0	0	3,119	3,097	22	23,018	18	23,000
Carbon Dioxide	0	36,652	36,652	55,885	2,162	53,723	17,071	19,808	313	19,492	2,475	2,473	2
Pounds/Pound EtO Product													
Nitrogen	4.980	10.664	15.644	15.644	0.013	15.631	4.967	4.967	0.002	4.965	0.015	0.015	0.0
Oxygen	1.513	0.758	2.271	1.113	0.002	1.111	0.353	0.188	0.0002	0.188	0.002	0.002	0.0
Ethane	0.006	0.013	0.019	0.019	0.0	0.019	0.006	0.006	0.0	0.006	0.0	0.0	0.0
Ethylene	1.014	0.446	1.460	0.657	0.003	0.654	0.208	0.093	0.001	0.092	0.004	0.004	0.0
Ethylene Oxide	0.0	0.0	0.0	0.877	0.877	0.0	0.0	0.125	0.124	0.001	1.001	0.001	1.000
Carbon Dioxide	0.0	1.466	1.466	2.235	0.086	2.149	0.683	0.792	0.013	0.779	0.099	0.099	NIL

NOTE: Numbers over columns refer to streams on Figure EO-1.

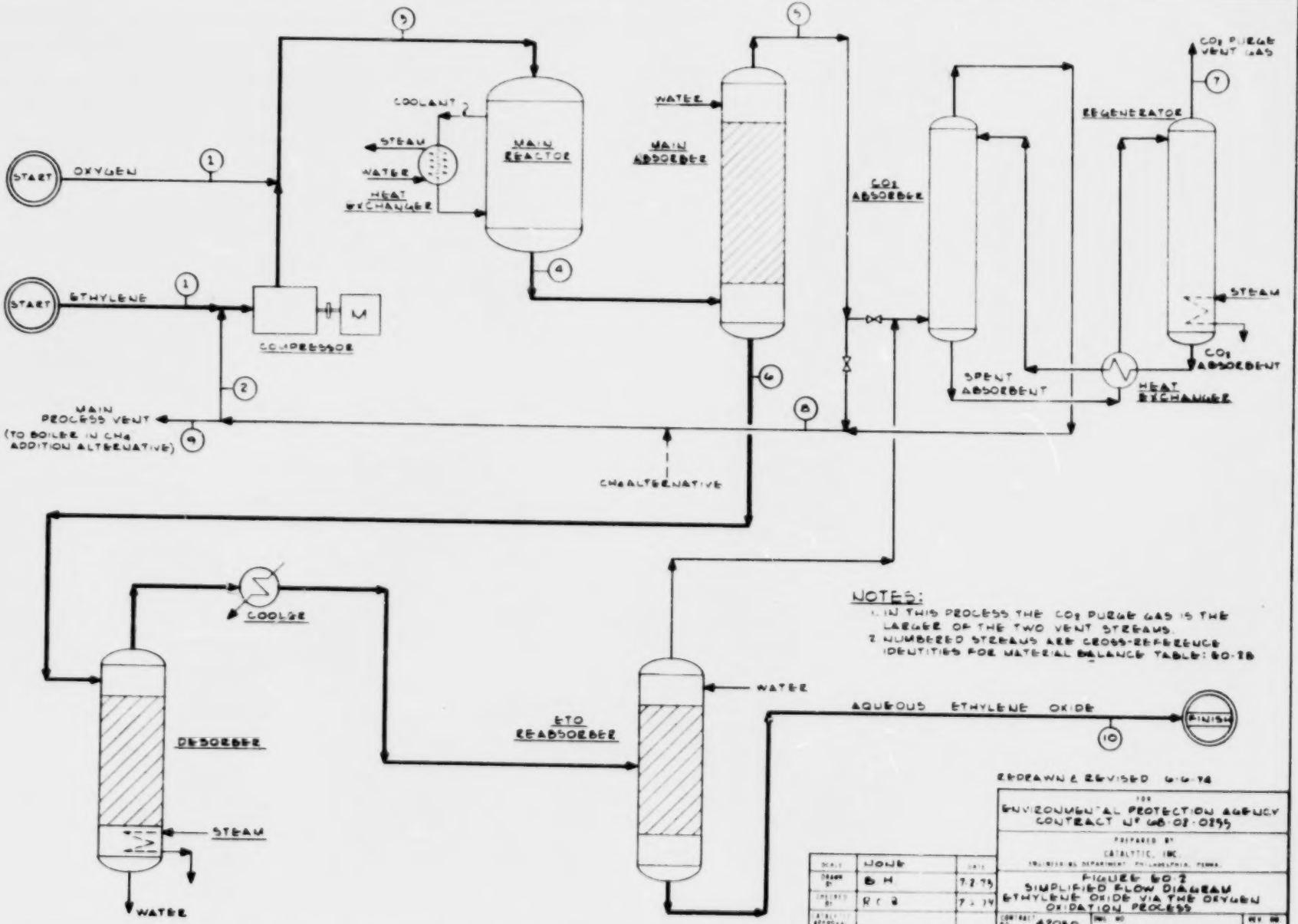
(1) Based on 8,000 hours per year operation.

(2) Dry basis.

The effluent gas from the primary reactor is cooled and compressed before entering the primary absorber which is generally operated with cold water. (If this absorber is operated with dilute sulfuric acid, recovery and hydrolysis to ethylene glycol take place simultaneously. No respondent indicated use of this system, however.) Absorbers using water are usually packed columns about 60 feet high. Feed to the absorber averages about 100° F. Ethylene oxide (the feed stream is about 1-2 mol % of ethylene oxide, 2-3% ethylene, plus CO_2, N_2, O_2 and A) in the effluent dissolves together with some CO_2 in the water. The aqueous stream is removed from the base of the absorber. Unabsorbed gas passing overhead is split into two portions. The larger portion of the gas stream is heat exchanged to raise its temperature and serves as the main stream for the secondary (purge) ethylene conversion system. Effluent from the secondary reactor is cooled and enters the purge absorber where ethylene oxide is removed from the stream with water. The overhead from this absorber, the main process vent, is oxide free and low in residual ethylene and is vented directly to the air or to a catalytic converter where the residual hydrocarbons are burned to heat the gas stream and the hot gas stream is used to drive the feed turbines for the process.

Dilute water solutions (containing EtO, CO_2 and traces of hydrocarbons) from both absorbers are combined. The mixture is fed to the top section of a bubble plate column where the absorbate is steam stripped under vacuum (desorbtion). Ethylene oxide is distilled off the top and is compressed for rectification. The bottoms water is recycled to the absorbers. Rectification of the ethylene oxide in the first distillation column removes the CO_2 and inert gases overhead (CO_2 rich purge gas). Ethylene oxide from the bottom of the column then feeds to the middle of a second distillation column for refining to 99+% purity. Product is stored under nitrogen or in refrigerated storage. Bottoms from the second column consist of water with traces of hydrocarbons. This stream is normally sent to in plant sewage treatment where it is biologically treated before release.

A material balance for a typical oxygen oxidation process is given in Table EO-2B. The process flow is very similar to the air oxidation process, except that there is usually only a primary reactor and absorber. Also, since the conversion of ethylene per pass is low (of the order of 10-15 percent), the recycle is larger than in the air process. Product recovery is similar on both processes but with the oxygen process a CO_2 absorber is required on a portion of the recycle stream to control the build up of CO_2. One modification that is practiced by at least one domestic operator of an oxygen oxidation process is to add methane to the recycle. This acts as an "inert" at the conditions of the process reactor but results in a vent gas that is suitable as boiler fuel, thus eliminating the need to vent residual traces of ethylene from the main process vent.



NOTES:

1. IN THIS PROCESS THE CO_2 PURGE GAS IS THE LARGER OF THE TWO VENT STREAMS.
2. NUMBERED STREAMS ARE CROSS-REFERENCE IDENTITIES FOR MATERIAL BALANCE TABLE: EO-2B

REDRAWN & REVISED 6-6-74

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT Nº 68-02-0299

PREPARED BY
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SUBSIDIARY OF CHEMICAL DEPARTMENT, PHILADELPHIA, PENNA.

FIGURE EO-2
SIMPLIFIED FLOW DIAGRAM
ETHYLENE OXIDE VIA THE OXYGEN
OXIDATION PROCESS

SCALE	NONE	DATE
DRAWN BY	B H	7-2-73
TRACED BY	R C B	7-3-74
FINAL APPROVAL		
APPROVED		7-8-74

CONTRACT NO. 42090
JOB NO. 519
DWG. NO. R-248
REV. NO. A

EO-7

TABLE EO-2B
TYPICAL MATERIAL BALANCE (1)
OXYGEN OXIDATION PROCESS
200 MM LBS./YEAR (2) ETHYLANE OXIDE

	1	2	3	4	5	6	7	8	9	10
Pounds/Hour	Fresh Feed	Recycle	Gross Reactor Feed	Reactor Effluent	Absorber Overhead	Absorber Bottoms	CO_2 Purge Vent (3)	Gross Recycle	Main Process Vent	Ethylene Oxide Product
Nitrogen, Argon	115	213,837	213,952	213,957	213,952	0	0	213,952	115	0
Oxygen	31,148	78,097	109,245	78,142	78,108	34	3	78,139	42	0
Methane	4	7,438	7,442	7,442	7,385	57	0	7,442	4	0
Ethane	95	143,178	143,273	143,273	143,195	79	18	143,255	77	0
Ethylene	22,417	126,443	148,860	126,531	126,359	172	70	126,511	68	0
Ethylene Oxide	0	74	74	25,074	74	25,000	0	74	0.04	25,000
Carbon Dioxide	0	698,155	699,155	719,333	712,422	6,911	19,800	699,531	376	2
Pounds/Pound EtO										
Nitrogen, Argon	0.005	8.553	8.558	8.558	8.558	0.0	0.0	8.558	0.005	0.0
Oxygen	1.246	3.124	4.370	3.126	3.125	0.001	Nil	3.126	0.002	0.0
Methane	0.001	0.297	0.298	0.298	0.296	0.002	0.0	0.298	0.001	0.0
Ethane	0.004	5.727	5.731	5.731	5.728	0.003	0.001	5.730	0.002	0.0
Ethylene	0.897	5.058	5.955	5.062	5.055	0.007	0.001	5.061	0.003	0.0
Ethylene Oxide	0.0	0.003	0.003	1.003	0.003	1.000	0.0	0.003	Nil	1.0
Carbon Dioxide	0.0	27.966	27.966	28.773	28.497	0.276	0.797	27.981	0.015	Nil

NOTE: Numbers over columns refer to streams on Figure EO-2

(1) Based on single questionnaire, dry basis.

(2) Based on 8,000 hours per year operation.

(3) Adjusted, from a single questionnaire, to include future changes as indicated on the questionnaire.

III. Producers of Ethylene Oxide and Emissions

The capacities and plant locations listed below are based on information provided in the questionnaires and in the literature.

Producer	Location	Capacity - MM Lbs./Yr.	Process (1)
BASF-Wyandotte	Geismar, La.	220	Shell
Calcasieu Chemical	Lake Charles, La.	165	Shell
Celanese	Bayport, Texas	300	Shell
Dow	Freeport, Texas Plaquemine, La.	1,000	Dow (2)
Eastman Chem. Prod.	Longview, Texas	50	Shell
Jefferson Chem. Co.	Port Neches, Texas	500	Scientific Design (2)
Koch Chemical	Orange, Texas	36	Scientific Design (2)
Northern Petrochemical	Joliet, Ill.	200	Scientific Design
Olin Corporation	Brandenburg, Ky.	100	Shell
PPG - Houston Chem.	Beaumont, Texas	80	Scientific Design (2)
Shell Chemical	Geismar, La.	300	Shell
Sun-Olin	Claymont, Del.	90	Shell
Union Carbide	Seadrift, Texas	700	Union Carbide (2)
	Taft, La.	450	Union Carbide (2)
		4,191	

(1) All plants use the direct oxidation of ethylene to ethylene oxide.
(2) Air oxidation.

Table EO-3 shows individual plant capacity figures and atmospheric emission data for the various ethylene oxide plants surveyed in the study. About 53 percent of the installed ethylene oxide capacity in the U.S. has been covered by this survey. Emissions from these plants are as follows:

A. Continuous Air Emissions

1. Main Process Vent Gas

This stream, which vents from the secondary or purge reactor absorber consists of "spent" air (N_2, O_2 and some inert gases), some CO_2, small to nil amounts of EtO and usually less than two percent hydrocarbons in an air oxidation plant. The similar stream from an O_2 oxidation plant has entirely different composition. Typical main process vent gases from both types of plants are shown on Tables EO-4A and EO-4B. This stream constitutes the largest emission of air pollutants from the process. Although dilute in concentration, the streams are large in volume and contribute over 50 percent of the total emissions.

2. CO_2 Rich Purge Gas

This is the overhead from the ethylene oxide rectification tower in the case of the air plants and the CO_2 system vent stream in the O_2 plants. The streams are not comparable in the two processes. Typical vent gas composition for this stream is also shown on Tables EO-4A and EO-4B.

TABLE EO-3
NATIONAL EMISSIONS INVENTORY
ETHYLENE OXIDE BY DIRECT OXIDATION

Plant EPA Code No.	13-1	13-2	
Capacity - Tons EtO/Yr.	350,000	100,000	
Range of Production - % of Max.			
Emissions to Atmosphere			
Stream	Absorber Waste Gas	Stripper Tail Gas	Reabsorber Vent Gas	Water Scrubber Vent Gas
Flow - Lbs./Hr.	116,352	1,096	3,671	682
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr.				
Composition - Ton/Ton EtO				
Oxygen		0.000356	0.000700	0.001660
Nitrogen, Argon	1.704736	0.001512		0.004582
CO_2		0.016624	0.137328	0.015036
Steam			0.002368	0.000043
NO_x				
C_1 - C_4 & Higher Hydrocarbons	0.049824	0.000739	0.006444	0.005952
Particulates				
Vent Stacks				
Number	1	1		
Height - Feet	50	52		
Diameter - Inches	24	2		
Exit Gas Temperature - °F	400	110	95	
SCFM/Stack	23,167	164	579	114
Emission Control Devices			None	None
Analysis				
Date or Frequency of Sampling	Continuous for EtO	Once per year	Daily	Never
Tap Location	Easy, Automatic	Easy	Easy, in line	No tap
Type of Analysis	GC, MS	GC, MS	GC	None
Odor Problem	No	No	No	No
Summary of Air Pollutants				
Hydrocarbons - Ton/Ton EtO		0.036117		0.012403
Aerosols - Ton/Ton EtO				
NO_x - Ton/Ton EtO				
SO_x - Ton/Ton EtO		Trace*		
CO - Ton/Ton EtO				
Type of Process	Air Oxidation		O_2 Oxidation	

*Fuel

TABLE EO-3
NATIONAL EMISSIONS INVENTORY
ETHYLENE OXIDE BY DIRECT OXIDATION

Plant EPA Code No.	13-3		13-7				13-4
Capacity - Tons EtO/Yr.	40,000		225,000				110,000
Range of Production - % of Max.			+4%				+4%
Emissions to Atmosphere							
Stream	Gas Turbine Exhaust	Reabsorber Vent Gas	Reactor Vent	Recovery System Vent Scrubber	Reactor Vent	Heater Vent	CO_2 Purge Vent
Flow - Lbs./Hr.	87,223	1,239	475,000	5,000	32.5	16	69,173
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr.							
Composition - Ton/Ton EtO							
Oxygen	0.52380	0.00262	0.045009	0.002362	0.000031		
Nitrogen, Argon	6.9775	0.020590	7.04927	0.019858	0.000755		
CO_2	1.0871	0.094750	1.23751	0.080533	0.000100		1.1610
Steam	0.13390	0.000360					1.5890
NO_x			0.000517				
C_1 - C_4 & Higher Hydrocarbons		0.005574	0.001270	0.008046	0.000047	0.00032	0.003217
Particulates		0.000053					
Vent Stacks							
Number	1	1	1	1			
Height - Feet	57	150	50	45			
Diameter - Inches	48	4	6' x 8'	4			
Exit Gas Temperature - °F	450	110	440	95			
SCFM/Stack	18,800	200	100,000	1,050			
Emission Control Devices							
Analysis							
Date or Frequency of Sampling	Never	2 per day	1 per hour	3 per year	Continuous	None	
Tap Location	Difficult	Easy	Easy	Bomb - difficult	Easy	None	
Type of Analysis			GC	MS	GC MS	Wt Balance	
Odor Problem	No	Yes	No	No	No	No	
Summary of Air Pollutants							
Hydrocarbons - Ton/Ton EtO		0.005574				0.008413	0.003755+
Aerosols - Ton/Ton EtO							
NO_x - Ton/Ton EtO						0.000517	
SO_x - Ton/Ton EtO						0.000229*	
CO - Ton/Ton EtO							
Type of Process	Air Oxidation		Air Oxidation				O_2 Oxidation

*Fuel gas.
+Includes .000538 fugitive $C_2^=$ losses.

TABLE EO-3
NATIONAL EMISSIONS INVENTORY
ETHYLENE OXIDE BY DIRECT OXIDATION

Plant EPA Code No.		13-5	
Capacity - Tons EtO/Yr.		100,000	
Range of Production - % of Max.			
Emissions to Atmosphere			
Stream	Gas Turbine Exhaust	Recovery Section Vent	Absorber Gas
Flow - Lbs./Hr.	76,000	3,100	5,500
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr.			
Composition - Ton/Ton EtO			
Oxygen	0.01578	0.001164	0.010748
Nitrogen, Argon	2.2660	0.01385	0.17920
CO_2	0.75550	0.10680	0.026284
Steam			
NO_x			
C_1 - C_4 & Higher Hydrocarbons	0.002764	0.002155	0.003768
Particulates			
Vent Stacks			
Number	1	1	
Height - Feet	45	35	
Diameter - Inches	30	4	
Exit Gas Temperature - °F	610	100	
SCFM/Stack	16,550	480	
Emission Control Devices			
Analysis			
Date or Frequency of Sampling	2 per month	2 per month (but EtO monitor continuously)	Certain components continuously
Tap Location	Easy, use Orsat bomb	Easy, automatic	Easy
Type of Analysis	GC	GC	GC
Odor Problem	No	No	No
Summary of Air Pollutants			
Hydrocarbons - Ton/Ton EtO			0.008687
Aerosols - Ton/Ton EtO			
NO_x - Ton/Ton EtO			
SO_x - Ton/Ton EtO			
CO - Ton/Ton EtO			
Type of Process	Air Oxidation		

TABLE EO-3
NATIONAL EMISSIONS INVENTORY
ETHYLENE OXIDE BY DIRECT OXIDATION

Plant EPA Code No.		13-6	
Capacity - Tons EtO/Yr.		18,000	
Range of Production - % of Max.			
Emissions to Atmosphere			
Stream	Cycle Gas Exhaust	Mix Gas Exhaust From Scrubber	Heater and Fuel Vents
Flow - Lbs./Hr.			
Flow Characteristic - Continuous or Intermittent			
if Intermittent - Hrs./Yr.			
Composition - Ton/Ton EtO			
Oxygen	0.35474	0.001728	
Nitrogen, Argon	5.84960	0.02219	
CO_2	0.91971	0.094720	
Steam	0.35182	0.000625	
NO_x			
C_1 - C_4 & Higher Hydrocarbons	0.06297	0.003819	0.001301
SO_x			0.000004
Vent Stacks			
Number			
Height - Feet			
Diameter - Inches			
Exit Gas Temperature - Fo			
SCFM/Stack			
Emission Control Devices			
Analysis			
Date or Frequency of Sampling	Occasional	Once per month	
Tap Location	Easy	Easy	
Type of Analysis	Orsat, CH	Orsat, CH	
Odor Problem	No	No	
Summary of Air Pollutants			
Hydrocarbons - Ton/Ton EtO			0.068090
Aerosols - Ton/Ton EtO			
NO_x - Ton/Ton EtO			
SO_x - Ton/Ton EtO			0.000004
CO - Ton/Ton EtO			
Type of Process	Air Oxidation		

TABLE EO-3

LIST OF ABBREVIATIONS IN ANALYSES Sheet 5 of 5

GC - Gas Chromatograph

MS - Mass Spectroscope

Orsat - Conventional orsat for CO_2, O_2, C_2H_4

CH - Ethylene oxide by reaction with $MgCl_2$ to form chlorohydrin

TABLE EO-4A
TYPICAL VENT GAS COMPOSITIONS
FOR
200 MM LBS./YR. ETHYLENE OXIDE PRODUCTION
USING AIR OXIDATION

MAIN PROCESS VENT GAS

Component	Avg. Mol %	Reported Range in Composition	Average Flow Rate Mol/Hr.	Lbs./Hr.
Nitrogen	86.7	80 - 90	4,695	131,460
Oxygen	2.9	0.5 - 4.5	157	5,024
Methane	0.0	0 - 0.9	0	0
Ethane	0.1	0 - 0.1	5	150
Ethylene	1.6	TR - 2.3	87	2,436
Ethylene Oxide	0.01	0 - 0.01	0.4	17
Carbon Dioxide	8.7	0 - 10	471	19,782
	100.00		5,415.4	158,869
	32,402 SCFM	29.3 Avg. Mol Wt.		

CO_2 RICH PURGE GAS

Component	Avg. Mol %	Reported Range in Composition	Average Flow Rate Mol/Hr.	Lbs./Hr.
Nitrogen	18	13 - 25	14.2	398
Oxygen	2	1 - 26	1.6	51
Ethylene	4.5	2.5 - 8.0	3.6	101
Ethylene Oxide	0.5	0 - 1.0	0.4	17
Carbon Dioxide	75	62 - 80	59.3	2,491
	100.0		79.0	3,058
	475 SCFM	38.7 Avg. Mol Wt.		

NOTE: Both streams on a water free basis.

TABLE EO-4B
TYPICAL VENT GAS COMPOSITIONS
FOR
200 MM LBS./YR. ETHYLENE OXIDE PRODUCTION
USING OXYGEN FEED

MAIN PROCESS VENT GAS (1,3)

Component	Mol %	Flow Rate Mol/Hr.	Flow Rate Lbs./Hr.
Nitrogen, Argon (MW = 39.2)	16.2	3.09	121
Oxygen	7.3	1.39	44
Methane	1.5	0.29	5
Ethane	14.2	2.70	81
Ethylene	13.5	2.57	72
Ethylene Oxide	0.005	0.001	0.04
Carbon Dioxide	47.4	9.02	379
	100.0	19.06	702
	114 SCFM	36.8 Avg. Mol Wt.	

CO_2 RICH PURGE GAS (1,2,3)

Component	Mol %	Flow Rate Mol/Hr.	Flow Rate Lbs./Hr.
Oxygen	0.02	0.1	3
Ethane	0.12	0.6	18
Ethylene	0.16	0.8	22
Carbon Dioxide	99.70	500.9	21,038
	100.00	502.4	21,081
	3,006 SCFM	42.0 Avg. Mol Wt.	

(1) Based on one questionnaire - other oxygen process does not have any appreciable vent other than CO_2 and water (one questionnaire). Methane is added after the reactors to build up a background of inert gas in the recycle strean at reactor conditions but a combustible gas at boiler conditions.

(2) Composition and quantity adjusted to include future changes as indicated on the questionnaire.

(3) Both streams on a water free basis.

3. Turbine Exhaust

Many, if not all of the plants surveyed use natural gas fueled turbines to feed air and ethylene to the process. Since the turbines which drive the compressors are not 100 percent efficient, some unburned hydrocarbons escape to the air from this exhaust. It can be a considerable portion of the total hydrocarbon emissions. A large variation in this stream has been reported (Table EO-3).

B. Intermittent Air Emissions

No data given although some plants report flaring or venting gas during upsets. One operator reported emptying the system to the flare one or two times per year for about three hours each time.

C. Liquid Wastes

Mainly water, with small percentage of organics, all of which appear to be adequately treated by conventional in-plant biologic systems for most respondents. One respondent reported inorganic salts (presumably from the CO_2 recovery section) in this stream.

D. Solid Wastes

None reported although one respondent alludes to the presence of about 0.004 lbs. of "sludge"/lb. EtO leaving the plant as part of the waste water stream. No further data were given.

E. Odors

Not one respondent reported any odor problem on any stream. The only reference to odor was the indication that, if there were an odor detectable, it would be ethylene. Actually this response is not surprising because:

1. The hydrocarbon content of the vast majority of all the vent streams is quite low.

2. Ethylene is a colorless sweet smelling gas. In low concentration, i.e., less than two percent, it is doubtful if one could detect an odor directly in the vent stream. As the vent gas mixes with the surrounding air, and the ethylene becomes more dilute, the possibility of an odor problem fades away. The absence of any detectable odor does not mean that there are no hydrocarbon emissions.

Ethylene oxide on the other hand has a pungent irritating odor. No one even so much as indicated an ethylene oxide odor problem. Again, not surprising. Ethylene oxide is the desired product and the odor of EtO means loss of a valuable commodity. To allow continuous loss of EtO would just not make good economic sense and any odor problem associated with ethylene oxide would be temporary and most probably due to a severe upset or equipment failure.

IV. Emission Control Devices and Systems

A. Emission Control Devices on Main Process Vent

1. Absorbers and Scrubbers

The main ethylene oxide absorber vent gas on all plants is recycled to the process. The secondary or purge absorber vent gas is normally the main process vent for the air oxidation plants and the oxygen feed plants. Two air oxidation process respondents catalytically convert this dilute hydrocarbon stream to N_2, CO_2, O_2 and H_2O and drive process tubines with the hot compressed gas. The other five respondents vent this stream to the air.

One of these latter plants (also air oxidation) supplied data on their purge absorber and it has been included on Table EO-5 for the sake of completeness. Actually all plants have this absorber-scrubber but only one gave data on it. Strictly speaking, it is a necessary process control device. It is identified as 002 on Table EO-5. Water is the absorbing medium.

Ethylene oxide absorbers/scrubbers do an excellent job in removing EtO from the off-gas stream. Efficiencies of 99.9+% are not uncommon. Ethylene oxide is very soluble in water and a well designed scrubber should perform well. However, a water scrubber will not remove any appreciable ethane or ethylene from the vent gas and as such this represents the major source of air pollution for the process. Unless this stream is catalytically combusted to CO_2 and water, it will contribute substantial quantities of hydrocarbons to the air in a stream generally too dilute to burn by itself.

Vent gas scrubbers using water to recover ethylene oxide are used by two respondents (see Table EO-5) on the CO_2 purge stream of air oxidation processes. Here again the efficiency of ethylene oxide recovery is good but efficiency is poor in terms of total hydrocarbon emissions. This CO_2 purge stream is the smaller of the two main vent streams.

2. Catalytic Conversion Units

These units are designed to convert the ethylene content (about two percent) of the absorber vent gas to CO_2 and water and to heat the gas stream at 100-200 PSIG from ambient temperature up to 1300° F. The gas is then used to drive a gas turbine and exhausts at about 600° F to a stack. Data on these units came from two air oxidation processes.

A typical catalyst would consist of activated precious metals (probably platinum) uniformly coated on a matting of high nickel chrome alloy metal ribbins. Self supporting catalyst mats are mounted in a hollow cylindrical configuration. The catalyst tube is surrounded by a cylindrical baffle that directs the incoming gas to the top of the vessel where gas burners preheat the gas to reaction temperature. The heated gas then passes over the catalyst where the ethylene reacts with the oxygen in the gas and heats the mass of the gas to about 1300° F. The converter outlet temperature controls the firing of the preheat burners.

TABLE EO-5
CATALOG OF EMISSION CONTROL DEVICES

ABSORBERS/SCRUBBERS

EPA Code No. for plant using	13.6	13.6	13.7
Flow Diagram (Fig. No) Stream I. D.	(EO-1)-10	(EO-1)-10	(EO-1)-10
Device I. D. No.	002	001	101
Control Emission of	Ethylene Oxide	Ethylene Oxide	Ethylene Oxide
Scrubbing/Absorbing Liquid	Water	Water	Water
Type - Spray			
Packed Column	X	X	
Tray Column			X
Scrubbing/Absorbing Liquid Rate - GPM	30	80	150
Design Temperature (Operating Temperature) °F	100	200	Ambient
Gas Rate - SCFM (lb./hr.)	300	6500	1167
T-T Height, Feet	32	57.5	40
Diameter - Feet	2	3.5	3.5
Washed Gases to Stack	Yes	Yes	Yes
Stack Height - Feet	62	38	45
Stack Diameter - Inches	3	8	4
Installed Cost - Mat'l. & Labor - $	Unknown	Unknown	24,000
Installed Cost Based on "year" - $			1968
Installed Cost - c/lb.			0.0053
Operating Cost - Annual - $ (1972)	Not Available	Not Available	$2500
Value of Recovered Product - $/Yr.			$225,000**
Net Operating Cost - c/lb.			(Credit - 0.049)
Efficiency - % - SE	99.99	98.5	95.3
Efficiency - % - SERR	97.05*	56.9*	66.2*

*For total hydrocarbons.
**For recovered EtO.

TABLE EO-5
CATALOG OF EMISSION CONTROL DEVICES (1)

INCINERATION DEVICES

EPA Code No. for plant using	13-3	13-4	13-5
Flow Diagram (Fig. No.) Stream I. D.	(EO-1)-10	(EO-2)-9	(EO-1)-10
Device I. D. No.	101		101
Type of Compound Incinerated	Hydrocarbons	Hydrocarbons	Hydrocarbons
Type of Device	Catalytic Converter	Flare Stack	Catalytic Converter
Material Incinerated, lb./Hr. (SCFM)	(20,000)	Normally Zero	76,000
Auxiliary Fuel Req'd. (excl. pilot)			
Type	CH_4		Natural Gas
Rate - BTU/Hr.	197×10^6		3×10^6
Device or Stack Height - Feet	57	125	45
Installed Cost - Mat'l. & Labor - $	$74,000		$300,000
Installed Cost Based on "year" - $	1984		1986
Installed Cost - ¢/lb.	0.0925		0.15
Operating Cost - Annual - $/Yr.	(Credit - $20,000)		$42,000
Operating Cost - ¢/lb.	(Credit - 0.025)		0.021
Efficiency - % - CCR	100	100 (2)	95.7
Efficiency - % - SERR	100	100 (2)	95.7

(1) Plant 13-7 also reported (subsequent to their completed questionnaire) a catalytic converter on the reactor vent shown in Table EO-1. However, they did not give cost or performance data on the unit.

(2) Flare shown as burning completely to CO_2 and H_2O.

The above is a description of one type of catalytic converter. There are other designs but they follow the general pattern described. In some case, it may be necessary to inject small quantities (roughly 0.4 mol %) of methane or natural gas plus some air in order to insure complete combustion in the converter. These units are rather large, seven to eight feet in diameter and 15 to 20 feet long.

Table EO-6 gives a material balance for catalytic incineration of a lean hydrocarbon vent stream. Section VII covers the cost effectiveness of this control. Actual cost data for catalytic converters are presented, as given by the respondents.

3. Other Combustion Devices

For those vent streams which are readily combustible, a steam boiler could be used to convert the hydrocarbon content to CO_2 and water and recover some of the waste heat as steam. Since ethylene oxide plants are net steam producers due to the exothermic heat of reaction, it may be uneconomical to run yet another steam boiler on a waste stream and have to transport the steam from the process area to where it can be used. In this case, a thermal incinerator could convert the vent gas stream to CO_2 and water and eliminate emissions of hydrocarbons to the air.

Only one respondent indicates use of the main process vent stream in a steam boiler but no operating data were given. This, of course, is the case where methane is added to the recycle. No one indicated use of a thermal incinerator so it is difficult to accurately predict equipment performance in these two applications. Table EO-7 and EO-8 give material and heat balance data for combustion of a fairly rich hydrocarbon vent stream. No data are included for thermal incineration or steam generation of a lean hydrocarbon stream (below the lower flammability limit) because such treatment is impractical and uneconomic.

4. Flare System

One respondent (oxygen oxidation process) reports on the use of a flare system (only during emergencies) and claims 100 percent efficiency. It was not reported whether or not supplemental fuel was used. Generally, a "flare system" is understood to mean a combustion stack that does not require supplementary fuel except for pilot lights. On the other hand, a plume burner is one which is burning a gas that is normally close to or below its lower flammable limit and thus requires a continuous supply of supplemental fuel. It is normally assumed that neither a flare stack nor a plume burner will achieve more than about 90 percent combustion efficiency.

The oxygen oxidation vent gas shown in Table EO-7 will support combustion and could be flared. However, it is unlikely that combustion would be complete. It is more likely that about 10 percent of the heating value will be lost in the form of carbon monoxide and unburned or cracked hydrocarbons. If the plant has an existing flare from another process, additional supplemental fuel might not be required, depending upon the heating value of total flared gases. In any case, however, improper firing could result in NOx formation.

TABLE EO-6
AIR FEED PLANT
CATALYTIC INCINERATION (1)

MATERIAL BALANCE, LB./HR.

Component	Process Vent Gas (2)	Combustion Air	Flue Gas (3)
N_2	131,858	14,663	131,858
O_2	5,075	4,457	212
CH_4	0	0	TR
C_2H_6	150	0	TR
C_2H_4	2,537	0	TR
EtO	34	0	0
CO_2	22,273	0	30,754
NOx (4)	6.4	0	6.4
H_2O	———	0	3,560
	161,933	19,120	181,053

(1) Combined combustibles are 1.67 percent by volume vs. 2.7 percent lean lower limit for ethylene in air. Catalytic incineration is necessary to hold combustion chamber temperature in the 1300° to 1500° range.

(2) Combined process stream, main vent plus CO_2 vent, water free basis.

(3) Unburned hydrocarbons reported as "trace" in flue gas. One respondent reported 200 to 300 ppm in flue gas but his vent gas stream differed from that shown above. Flue gas has 0.5 percent excess O_2 as per respondnet experience with catalytic converters.

(4) 40 ppm.

TABLE EO-7
OXYGEN FEED PLANT, STEAM GENERATION
OVERALL MATERIAL BALANCE, LB./HR.

Component	Process Vent Gas (2)	Combustion Air (1)	Flue Gas
N_2, A	121	2,102	2,223
O_2	44	639	114
CH_4	5	0	TR
C_2H_6	81	0	TR
C_2H_4	72	0	TR
EtO	0.04	0	TR
CO_2	379	0	827
NOx	0	0	TR
H_2O	—	0	250
	702	2,741	3,444

(1) 20 percent excess O_2.

(2) Water free basis combined combustibles are 27.6 percent well over the lower limit for ethylene. This stream will support combustion.

Other Data - Heat Balance

a. Heat of combustion of methane, ethane, ethylene in stream - 3,221,078 BTU/Hr.

b. Less sensible heat, 85° ⟶ 570° (stack temperature) - 439,020 BTU/Hr.

c. Net heat available for steam generation 2,782,058 BTU/Hr.

d. Steam available at 750° F, 450 PSIG at 75c/1000 lbs., credit is $14,850 per year 2,261 Lbs./Hr.

TABLE EO-8
OXYGEN FEED PLANT
THERMAL INCINERATION
MATERIAL BALANCE

This same stream when thermally incinerated with 20 percent excess O_2 will give the same products of combustion as a steam generator but the heating value of the stack gas will be lost.

An incinerator for this stream will cost less than half of a comparable steam generator but the net operating cost is some 25 percent higher. See Table EO-7.

B. CO_2 Rich Purge Gas

This stream, which averages around 300 SCFM for a typical 200 MM lbs./year plant, is normally vented directly to the air by all respondents. For air oxidation plants, the stream contains about 70 vol. % CO_2 and 5-6% hydrocarbons and can be incinerated. The best solution would be to combine this vent stream with the main process vent stream since it is a small flow and dispose of both streams together. One respondent plans to do just this, feeding the CO_2 rich stream to a catalytic converter along with the main process vent and virtually eliminating emissions from the plant.

For the oxygen feed plants, this stream contains water vapor, 30-50 percent CO_2 and only traces of hydrocarbons. Hence, these plants probably have no need to treat this stream any further. One respondent usually disposes of this stream by selling it to an off-site consumer for its carbon dioxide content, but what is done with the hydrocarbon content is un-reported.

C. By-Product Disposal

1. Waste Water

From 0.007 to 0.9 gallons of waste water per lb. ethylene oxide are produced with the larger plants consuming the least water/lb. product. Data on contaminants in the waste streams are very sketchy but are probably ethylene glycol (mainly) acetaldehyde and miscellaneous hydrocarbons. All respondents, save one, treat this stream in plant before discharge. This stream is biodegradable and presents no unusual operating problems.

2. Waste Solids

No waste solids were reported.

3. Miscellaneous

No other by-products were reported.

D. Best Available Pollution Control System

The best control system for an air oxidation ethylene oxide plant is to feed both the main process vent and the CO_2 purge vent to a catalytic converter and use the hot gases from this unit to power feed turbines to the process. With this set-up, emissions from the plant vent streams should only be N_2, O_2, CO_2 with possible traces of hydrocarbons and NOx. The questionnaires indicate that several plants are planning to install this type of system. Oxygen feed plants are different than air feed plants because the CO_2 purge vent which is reported as essentially hydrocarbon free, is the larger stream, and probably can be vented directly to the air with little or no effect on the pollution level. It is also apparently pure enough to be sold as CO_2. The main process vent from these plants is small but is combustible. It can best be disposed of by burning in a steam generator with recovery of the heat as steam. If steam is not needed and the gas cannot easily be transported elsewhere, it may be disposed of in a thermal incinerator with a similar reduction in emissions as the steam generator, but with no energy recovery.

One of the air oxidation processes features introduction of methane as an "inert" background gas in the recycle stream in contrast to other oxygen processes which have no methane addition. The relatively rich main process vent gas from these plants can be sent to the plant boilers as supplemental fuel, even though the methane does not oxidize at reactor conditions.

Whether or not the CO_2 purge vent from either type of oxygen plant can be vented should be dtermined by an EPA sampling program. If not, it could constitute a problem because it is too large to be combined with the main process vent for incineration either in the plant boiler, the steam generator or the thermal incinerator. The dilution effect would render the combined stream non-combustible.

V. National Emission Inventory

Based on the emission factors shown in Table EO-3, the total emissions from the ethylene oxide plants surveyed were estimated and are summarized in Table EO-9. Using Table EO-9, the total approximate emissions from all U.S. ethylene oxide plants are as follows:

Component	Average Emissions T/T Ethylene Oxide	Total Emissions (1) MM Lbs./Year
Hydrocarbons	0.02048	85.83
Particulates	0.000007	0.03
NOx	0.000066	0.28
SOx	0.000031	0.13
	Total = 0.020584	86.27

If all air feed plants catalytically converted their main process vent gases to CO_2 and H_2O and used the hot exhaust to drive the plant feed turbines, (also cutting the turbine emissions about in half) and oxygen feed plants incinerated their main process vent in a steam generator, total emissions would be reduced to the following approximate values:

Component	Average Emissions (2) T/T Ethylene Oxide	Total Emissions (1) MM Lbs./Year
Hydrocarbons	0.0049	20.53
Particulates	0.000007	0.03
NOx	0.0001	0.42
SOx	0.000031	0.13
	Total = 0.005038	21.11

(1) Basis 4,191 MM lbs. EtO per year in 1972.
(2) See also Table EO-16.

TABLE EO-9
EMISSION SOURCE SUMMARY
TON/TON ETHYLENE OXIDE
AIR OXIDATION PLANTS

Emission	Source							Total
	EtO Absorber Vent Gas	Recovery Section Vents	Vent Gas Scrubber Outlet	Turbine Exhaust	Reactor or Heater Vent	CO_2 Purge Vent	Figitive Emissions	
Hydrocarbons	0.0118	0.0006	0.0023	0.0132	0.0006	0.00001	0.00001	0.0285
Particulates			0.00001					0.00001
NOx					0.0001			0.0001
SOx					0.00005			0.00005
CO								

OXYGEN OXIDATION PLANTS*

	Reabsorber Vent Gas	Water Scrubber Vent	Total
Hydrocarbons	0.0064	0.0060	0.0124
Particulates, NOx	Nil	Nil	Nil
SOx, CO	Nil	Nil	Nil

OXYGEN OXIDATION PLANTS WITH METHANE ADDITION*

	CO_2 Purge Vent	Fugitive Losses	Total
Hydrocarbons	0.0032	0.0006	0.0038
Particulates, NOx	Nil	Nil	Nil
SOx, CO	Nil	Nil	Nil

*Data from one respondent only.

VI. Ground Level Air Quality Determination

Table EO-3 presents a summary of air emissions data for various surveyed ethylene oxide plants. This table includes emissions from the main process vent, CO_2 purge vent, turbine exhausts, reactor heat transfer fluid vent and an estimate of fugitive emissions. Information regarding vapor losses from product storage have not been included, but losses from these storage facilities should be low for the following reasons:

(a) All plants reporting data on their storage facilities have refrigerated, cooled and/or pressure (inert blanket) storage for ethylene oxide. Hence, emissions should be negligible. One plant blankets the ethylene oxide with natural gas to prevent loss of EtO. The blanketing gas usually goes to a flare when the tank "breathes". A loss of blanketing gas is unavoidable but will contribute virtually no air emissions if it is flared properly.

(b) Some plants take ethylene oxide directly to a glycol plant and as such have no storage facilities for this product.

Table EO-3 provides operating conditions and physical dimensions of the various vent stacks. The EPA will use this information together with the air emission data to calculate ground level concentration for later reporting.

VII. Cost Effectiveness of Controls

A cost analysis for alternative methods of reducing air pollution from the main process vents of a typical 200 MM lbs. per year ethylene oxide plant is shown on Tables EO-10 and EO-11. Table EO-10 represents data from plants using air feed while Table EO-11 shows similar data for oxygen oxidation plants.

A. Investment

Purchased costs of steam generators, thermal incinerators and catalytic incinerators were obtained from current vendor quotes for similar packaged type units. Costs for the catalytic converter represent actual dollars reported from respondents questionnaire up-dated to 1973.

B. Operating Expense

Unless data were available from the respondent, we used:

1. Depreciation - 10 year straight line.
2. Interest - 6 percent on total capital
3. Maintenance - 3 percent of investment.
4. Labor - One-quarter of a man assumed for boilers (steam generator) and one-eighth man for incinerators.
5. Utilities - Based on the Gulf Coast area.

The tables show that if the steam can be used, a steam generator is a cheaper method to use than a thermal incinerator for an oxygen oxidation process. A properly designed thermal incinerator has the advantage over a flare in that less NOx should be produced. It steam could not be used or transported to other process areas economically, a thermal incinerator would be the best method to use to reduce emissions.

However, the air process vent streams are not readily combustible. In this case, the best solution appears to be to catalytically incinerate the vent gas. Two respondents indicated that this was done with the main process vent gas. The hot gases from the converter (catalytic incinerator) are used to drive the process air compressor turbine drives. The literature says that almost every manufacturer uses these gases to drive turbines for the plants but if so, only two respondents so indicated and gave supporting engineering data.

If one take credit for the heating value of the gas burned which is used to power some of the process feed turbines, the analysis shows that this cost savings will just about off-set the operating and capital charges for a catalytic converter in a 200 million lbs./year ethylene oxide plant.

All plants reporting store ethylene oxide either under refrigeration or pressure (N_2, natural gas). All have vapor conservation systems and none vent to the atmosphere directly. As such, there does not appear to be anything further necessary for the storage facilities.

TABLE EO-10
COST EFFECTIVENESS OF CONTROLS
AIR OXIDATION PROCESS

Chemical	Ethylene Oxide		
Total U. S. Installed Capacity, Tons/Yr. (a)	2,100,000		
Total U. S. Production, Tons/Yr. (a)	2,100,000		
Principal Process	Air Oxidation		
Percentage of Total U. S. Production, Approximate	%		
Average Plant Capacity, Tons/Yr.	100,000		
Emission Stream	Main Process Vent		CO_2 Rich Purge (as
Emission Control Device	None	Catalytic (f) Incineration	None	Catalytic Incinerator (e)
Flow Rate, SCFM, Basis Average Plant Size	32,402		480	
Ton/Ton Ethylene Oxide Capacity				
NO_x	None	None	None (b)	TR
SO_2	None	None	None	None
CO	None	None	TR	None
CO_2	0.88645	1.22255	0.10911	0.12448
N_2 + Argon	5.75796	6.35093	0.01743	0.06675
O_2	0.22005	0.00858	0.00230	0.00070
H_2O	(j)	0.14962	(j)	0.00631
Misc. HC	0.11327	TR	0.00442	TR
Unidentified Particulates	None	None	None (d)	None
Ethylene Oxide	0.00074	TR	0.00074	TR
Installed Cost Relative to Emission Control Device				
Delivered Cost		$158,000		$12,000
Installation		67,000		8,000
Total Capital		$225,000		$20,000
Operating Cost, $/Yr.				
Depreciation (10 years)		$ 22,500		$ 2,000
Interest on Capital (6%)		13,500		1,200
Catalyst Replacement (estimated)		5,000		500
Maintenance (3% of capital)		6,800		600
Labor ($4.85/man-hour)		4,900 (1/8 man)		
Utilities				
Power, 1c/KWH		200		200
Fuel, 40c/MM BTU (pilot gas)		500 (c)		500 (c)
Process Water, 10c/M Gal.		0		0
Boiler Feed Water, 30c/M Gal.		0		0
Total Utilities		$ 700		$ 700
Total Operating Costs		$ 53,400		$ 5,000
Heating Value Credit (g)		50,000		1,000
Net Operating Cost		$ 3,400		$ 4,000

(a) Estimate for 1973.
(b) Exception - one respondent reports 40 PPM NO_x in a vent containing no other pollutant vapors.
(c) Heat exchange incorporated for sustained oxidation; pilot only during portion of start-up sequence. Start-up fuel required.
(d) Exception - one respondent reports "less than three lbs./hr. (of particulates), primarily carbon, small quantities of iron and chlorine".
(e) Incineration figures are estimated for addition of facilities where none exist in current practice. The inclusion of these figures is not to be construed as an indication that the facilities should or should not be installed.
(f) Data from two respondents showed about $85,000 purchased cost in 1964 - 1966, updated to $150,000 in 1973 and estimated $225,000 installed cost.
(g) Credit of 0.025c/lb. of EtO/year taken from net heating value of gas burned and used to power turbines.
(h) Streams are below lean lower limit for combustion. Thermal incineration or incineration in a steam boiler would require excessive firebox temperatures for complete combustion.
(i) Installed cost based on data from two respondents. Corrected to 200 million lbs./year via the "0.6 factor" and up-dated from 1965 costs using O&GJ Construction Cost Index.
(j) Main Process Vent and CO_2 Vent on water free basis.

TABLE EO-11
COST EFFECTIVENESS OF CONTROLS
OXYGEN OXIDATION PROCESS

Chemical		Ethylene Oxide		
Total U. S. Installed Capacity, Tons/Yr. (a)		0.5 MM		
Total U. S. Production, Tons/Yr. (a)		0.5 MM		
Principal Process		Oxygen Oxidation		
Percentage of Total U. S. Production, Approximate		24		
Average Plant Capacity, Tons/Yr.		100,000		
Emission Stream	CO_2 Rich Purge Gas	Main Process Vent		
Emission Control Device	None	None	Steam Generator (c)	Thermal Incinerator (c)
Flow Rate, SCFM Average Plant Size	5,782	699		702
Ton/Ton Ethylene Oxide Capacity			(b)	(b)
NO_x	None	None	TR	TR
SO_2	None	None	None	None
CO	None	None	TR	TR
CO_2	0.92147	0.01660	0.03622	0.03622
N_2 + Argon	None	0.00530	0.09737	0.09737
O_2	0.00013	0.00193	0.00499	0.00499
H_2O	(e)	(e)	0.01095	0.01095
Misc. HC	0.00096	0.00692	TR	TR
Unidentified Particulates	None	None	None	None
Ethylene Oxide	None	TR	None	None
Installed Cost Relative to Emission Control Device				
Delivered Cost			20,000	8,000
Installation			20,000	8,000
Total Capital			40,000	16,000
Operating Cost, $/Yr.				
Depreciation (10 years)			4,000	1,600
Interest on Capital (6%)			2,400	1,000
Catalyst Replacement (Estimated)			0	0
Maintenance (3% of capital)			1,200	500
Labor ($4.85/man-hour)			9,700 (2 man)	4,900 (1/8 man)
Utilities				
Power, 1¢/KWH (estimated)			200	100
Fuel, 40¢/MM BTU (pilot gas)			1,500	1,500
Process Water, 10¢/M Gal.			0	0
Boiler Feed Water, 30¢/M Gal.			700	0
Total Utilities			2,400	1,600
Total Operating Costs			19,700/Yr.	9,600/Yr.
Steam Generation, 75¢/M Lbs. (credit)			($13,800/Yr.)	
Net Operating Costs			5,900/Yr.	9,600/Yr.

(a) Estimated for 1973.
(b) Basis 20% "excess air".
(c) Steam generation and incineration figures are estimated for addition of facilities where none exist in current practice. The inclusion of these figures is not to be construed as an indication that the facilities should or should not be installed.
(d) Cost of steam generator and thermal incinerator from A.P.C.I. (Catalytic, Inc.) company files.
(e) Vents on water free basis.

VIII. Source Testing

Plants 13-3 and 13-5 were the only plants that reported a catalytic converter in operation when the questionnaires were completed. Data from these two plants indicate that a catalytic converter is an excellent pollution control device. If the data presented by these respondents can be substantiated by a sampling program and if the hydrocarbon emission reduction is as complete as is claimed, this device could be classified as the best demonstrated emission control system. It has since been reported by an official of plant 13-7 that they also have a catalytic converter, although this was not clear from the questionnaire.

Respondent 13-4 shows one stream which is quite rich in hydrocarbons as going to a steam generator. (No data on operation of this unit were given.) The stream is burned to generate steam used elsewhere. It would not be valuable to source test this stream as it represents a unique process, because methane is fed into the process streams to build up an inert background gas in the recycle. However, since this plant is an oxygen feed plant and reports very low hydrocarbons in the CO_2 purge gas vent, a sampling program to verify this could be of value.

IX. Industry Growth Projection

Current U.S. capacity for ethylene oxide production is estimated at 4,191 MM lbs./year and is projected to increase to 6,800 MM Lbs./year by 1985. (See Figure EO-3)

By far, the largest use for ethylene oxide is in the production of ethylene glycol. Probably two-thirds of all the ethylene oxide produced goes into glycol manufacture. Ehylene glycol's largest, but slowest growing end use is anti-freeze which accounts for about 70 percent of the ethylene glycol produced. Another area of increased use of glycol is in polyester fiber and film production.

The second largest market for ethylene oxide is nonionic surface-active agents which consume 10-15 percent of the ethylene oxide production. Ethoxylated mixed linear alcohols (components in biodegrabable detergents) have been the major contributor to this use of ethylene oxide in recent years.

Glycol ethers, the third largest end use of ethylene oxide has exhibited the fastest rate of growth as a consumer of the oxide. Most of this growth can be attributed to the use of ethylene glycol monomethyl ether as a jet fuel additive.

Ethanolamines follow glycol ethers as the next largest consumer of ethylene oxide. The fastest growing use for these ethanolamines has been in the manufacture of surface active agents, e.g., diethanolamine condensates of conconut oil acids and lauric acid.

Fifth in size of ethylene oxide consumption is diethylene glycol whose major end use is in polyurethane and unsaturated polyester resins.

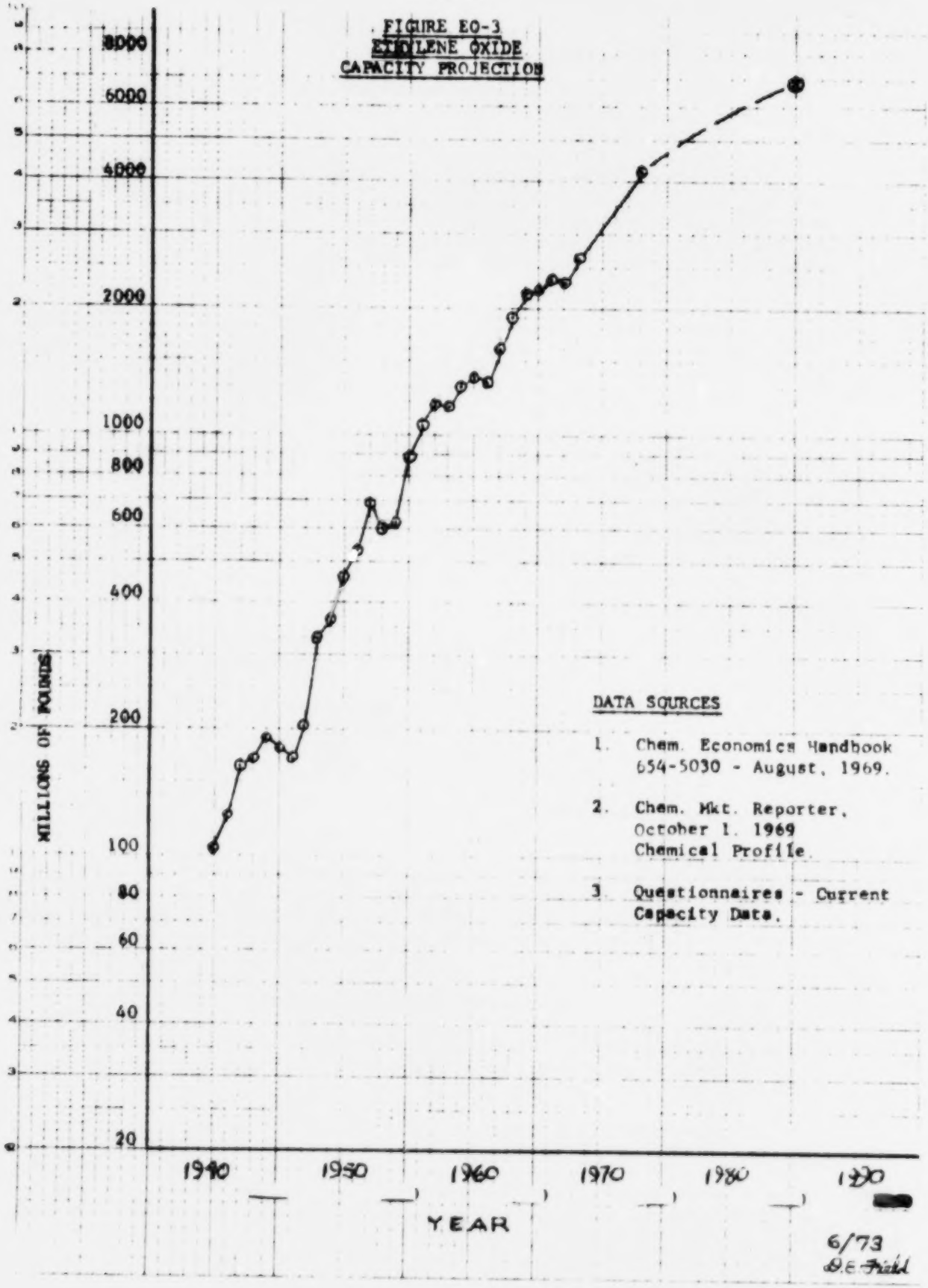
Ethylene oxide is also consumed in the manufacture of numerous other chemicals such as ethyl acrylate, choline and choline chloride, acrylonitrile (probably not being used commercially now), hydroxyethyl cellulose, hydroxyethyl starch, polyethylene oxide resins, fumigants and food sterilants.

A conservative growth rate for ethylene oxide through 1985 of four percent per year has been estimated. It is based mainly on Figure EO-3 which shows the growth of ethylene oxide production since 1940. In the early 1970s, by far the dominant process has been direct oxidation as opposed to the older chlorohydrin process. All new growth has been projected to be via the direct oxidation route. A good average plant size is 200 MM lbs./year and as such about 15 new units will have to be built between now and 1985. (See Table EO-12)

The price history of ethylene oxide is interesting. From 1940 to the mid fifties, it showed a small increase each year until the direct oxidation process really began to catch on. From 1955 to the present, there has been a steady drop in price from 15¢/lb. to 7.5¢/lb. in mid 1973 despite a general rise in prices in the economy.

The chlorohydrin process is only economic when the price of ethylene is greater than six times that of the chlorine price and is also more economical when ethylene oxide prices are high. At low ethylene oxide prices, the direct oxidation route gives a better return on ethylene and with low ethylene prices, the direct oxidation process has completely taken over the production of ethylene oxide.

FIGURE EO-3
ETHYLENE OXIDE
CAPACITY PROJECTION



DATA SOURCES

1. Chem. Economics Handbook 654-5030 - August, 1969.
2. Chem. Mkt. Reporter, October 1, 1969 Chemical Profile.
3. Questionnaires - Current Capacity Data.

6/73
D.E. Field

TABLE EO-12
NUMBER OF NEW PLANTS BY 1985

Current Capacity	Marginal Capacity	Current Capacity On-Stream in 1975	Demand 1985	Capacity 1985	Capacity to be Added	Economic Plant Size	Number of New Units
4,191	356	3,835	6,800	6,800	2,965	200	15

NOTE: All capacities in millions of pounds per year.

X. Plant Inspection Procedures

The largest source of emissions from an ethylene oxide plant would be hydrocarbons, chiefly ethylene. These hydrocarbon emissions are sometimes vented as a very dilute stream of hydrocarbons in a large amount of nitrogen, CO_2 and some oxygen. The vented gas stream should be below the lower explosive limit of ethylene in air.

A. There is no easy way to test for the presence of hydrocarbons in an air-CO_2 stream other than a chromatograph and this is not generally a portable instrument. A quick, albeit rather qualitative test for the presence of ethylene is odor. There should be no odor detectable. Ethylene has a sweet odor and taste but it is not a strong odor. Ethylene has no local or chronic irritant rating. If the odor of ethylene is detectable, the unit is probably upset and venting improperly. The normal two percent ethylene $\pm$ one percent in the vent gas probably will not be detectable by smell. The absence of any sweet odor does not mean that there are zero emissions.

B. Ethylene oxide, on the other hand, is quite detectable by odor. It is irritating to the eyes and nose and is classified as an acute local irritant. In high concentrations, it numbs the sense of smell. It is toxic and should not be inhaled although it is non-cumulative in the body and is not a chronic poison. If the odor of ethylene oxide is detectable, chances are that the purge reactor absorber (or the secondary absorber/scrubber) is upset and not functioning properly. If would be advisable to discuss the following with plant officials.

1. Proper flow of absorbing medium - water.

2. Proper temperature of the absorbing medium and the scrubber.

3. Deposits of material on the packing of the absorber which could foul the scrubber internally and cause by-passing.

4. Markedly different temperature and pressure of the feed gas to the scrubber than design.

Since ethylene oxide is the desired product and is being recovered in rather dilute form from the reactor effluent gases, prudent management of the plant would insist that every bit of ethylene oxide be recovered. It is just not economical to lose ethylene oxide due to improper scrubber operations so these instances should be rare.

C. Stacks should be checked for particulate emission and NOx by opacity. All stacks should be practically colorless but again a clear stack does not mean no hydrocarbon emissions because ethylene and related compounds are colorless.

D. Flares, if any, should be smokeless and only a rather substantial upset should cause smoke here. However, putting a dilute stream of hydrocarbons through a flare below the lower combustible limit of the stream will result in a clean flare but no reduction in hydrocarbon emissions.

E. Incinerators - If thermal incinerators are provided on any of the vent streams, a visual check of the stack gas should be made. The

stack should be nearly clear, if not completely clear. Since the feed stream to the incinerator is liable to be below its combustible limit, one should check to see if adequate supplemental fuel is being burned to properly combust the vent gas. Design specifications should be compared to actual operating conditions since there probably will be no visible clue in the stack effluent. Some check points would be:

1. Burner in the combustion zone should be operating.

2. Combustion zone temperature in the design range.

3. Stack gas temperature in the design range.

4. Process gas valves open to the incinerator.

A catalytic incinerator or converter may also be used. In fact, this type of device is more likely to be encountered than a thermal incinerator. Generally, the off-gas from the converter will be used to power a turbine before exhausting to the air. The same points should be checked on the catalytic converter as on the thermal incinerator. Supplemental fuel may or may not be used on a catalytic incinerator.

Log data on operation of both types of incinerators should be reviewed, especially if stack gas analyses are available via a chromatograph and recorded intermittently or continuously. Hydrocarbons in the stack gas should be virtually nil (say 0.2 percent or less and zero if possible).

XI. Financial Impact

Table EO-13 presents an estimate of the cost of ethylene oxide manufacture by both an air oxidation process and by an oxygen oxidation process. The difference in manufacturing cost may not be as great as the table shows at 200 MM lbs./year (i.e., the 0.48¢/lb. may be on the high side) but the literature indicates a small advantage for the air process at capacities over about 100 MM lbs./year, a break even at 60-70 MM lbs. and a small edge for the O_2 process in smaller plants. The minimum economical plant size is reported to be about 25 MM lbs./year.

Table EO-14 was calculated by using the air oxidation process as outlined in Table EO-13, but adding emission control facilities to reduce hydrocarbon venting to near zero with a catalytic converter on the two main process streams. This represents the most feasible new air oxidation facility at 200 MM lbs. per year production and virtually no emissions. Credit for power derived from the incinerator gases was taken as 0.25¢/lb., based on data in the questionnaires. Cost of building a new 200 MM lbs./year air oxidation ethylene oxide plant with good pollution control facilities would reduce profits after taxes by about 1.5 percent.

Table EO-15 was calculated by using the oxygen oxidation process as outlined in Table EO-13, but adding emission control facilities to reduce hydrocarbon venting to near zero with an incinerator and steam generator. This represents the most feasible new oxygen oxidation facility at 200 MM lbs./year production and virtually no emissions. Net operating cost is only $5,900/year. Cost of building a new 200 MM lbs./year oxygen oxidation ethylene oxide plant with good pollution control facilities would reduce profits after taxes by about eight percent.

A sensitivity analysis was performed for the catalytic incineration installation in the air oxidation process (Table EO-14b). Installed cost of the pollution control facility was varied $\pm$ 50 percent and its effect on the R.O.I. calculated. The 6.8 percent R.O.I. was found to vary from 6.5 to 7.1 percent.

A comparable calculation on the operating cost sensitivity would result in variations of similar magnitude because the savings in operating costs through the addition of a catalytic converter are approximately equal to the increased capital charges. If both sensitivities were applied simultaneously, they sould nearly off-set each other.

Sensitivities were not calculated for the oxygen oxidation process because the extra capital involved is only $40,000 on a $5,200,000 plant and the extra operating cost is only $20,000/year on a $14,540,000/year total. Thus, it was judged that the sensitivities are not significant.

Table EO-16 is a pro-forma balance sheet for the two above cases. A constant selling price of 7.5¢/lb. for ethylene oxide was used. Capital requirements for the most feasible new plants are about $225,000 higher with air oxidation and about $40,000 higher with oxygen oxidation than for existing type plants.

In addition to the financial impact of the proposed most feasible new plants a definite positive environmental impact would result. Not only would 2,050 tons of hydrocarbons per 200 MM lbs./year plant not be vented to the atmosphere (for 1985, 15 new plants would vent 30,750 tons of hydrocarbons per year if not controlled) but an energy savings could be realized

if the hot gases were used to drive some of the process turbines or generate steam.

For 1985, installation of emission control facilities and utilization of the power generated would be equal to a savings of about three billion cubic feet of gas per year.

TABLE EO-13
ETHYLENE OXIDE MANUFACTURING COST*
FOR A TYPICAL
EXISTING 200 MM LB./YR. FACILITY

PROCESS	O_2		AIR	
DIRECT MANUFACTURING COST	¢/LB.	$/YR.	¢/LB.	$/YR.
Raw Materials				
Ethylene (4.0¢/lb.)	3.8		3.8	
Oxygen ($15/ton)	1.0		0.0	
Catalyst & Chemicals	0.2		0.2	
Labor	0.31		0.31	
Maintenance @ 5% of Investment	0.13		0.25	
Utilities	0.60		0.60	
	6.04		5.16	
INDIRECT MANUFACTURING COST				
Plant Overhead @ 110% of Labor	0.34		0.34	
FIXED MANUFACTURING COST				
Depreciation - 10 year str. line	0.26	520,000	0.50	1,000,000
Insurance & Prop. Tax 2.3% of Inv.	0.06		0.11	
	0.32		0.61	
MANUFACTURING COST	6.70		6.11	
GENERAL EXPENSES				
Administration (3% of Mfg. Cost)	0.20		0.18	
Sales (1% of Mfg. Cost)	0.07		0.06	
Research (2% of Mfg. Cost)	0.13		0.12	
Finance (6% of Investment)	0.15		0.30	
TOTAL COST	7.25	14,500,000	6.77	13,540,000
PRODUCT VALUE				
Ethylene Oxide @ 7.5¢/lb.		15,000,000		15,000,000
Profit before Taxes		500,000		1,460,000
NPAT (52%)		240,000		700,800
Cash Flow		760,000		1,700,800
ROI		4.6%		7.0%

*Taken from literature "Petrochemical Industry: Markets & Economics" up-dated and scaled up to 200 MM lbs./year using "0.6 Factor" on capital for both O_2 and Air Feed Plants. Based on 1973 dollars.

TABLE EO-14
ETHYLENE OXIDE MANUFACTURING COST*
FOR NEW PLANT WITH CATALYTIC INCINERATION
200 MM LBS./YR. FACILITY

AIR OXIDATION PROCESS

DIRECT MANUFACTURING COST	¢/LB.	$/YR.
Raw Materials		
Ethylene	3.8	
Catalyst & Chemicals	0.2	
Labor	0.31	
Maintenance	0.255	
Utilities	0.575	
	5.140	
INDIRECT MANUFACTURING COST		
Plant Overhead (110% of Labor)	0.34	
FIXED MANUFACTURING COST		
Depreciation - 10 year straight line	0.51	1,020,000
Insurance & prop. Tax (2.3% of Investment)	0.12	
	0.63	
MANUFACTURING COST	6.11	
GENERAL EXPENSES		
Administration - 3% of Mfg. Cost	0.18	
Sales - 1% of Mfg. Cost	0.06	
Research - 2% of Mfg. Cost	0.12	
Finance - 6% of Investment	0.31	
TOTAL COST	6.78	13,560,000
PRODUCT VALUE		
Ethylene Oxide @ 7.5¢/lb.		15,000,000
Profit before Taxes		1,440,000
NPAT (52%)		691,200
Cash Flow		1,711,200
ROI	6.8%	

*Cost of catalytic converter taken from questionnaire data updated and corrected to a 200 MM lbs/year plant. Other costs from Table EO-13. (1973 dollars)

TABLE EO-14A
SENSITIVITY ANALYSIS
AIR OXIDATION PLANT WITH
CATALYTIC CONVERTER AND ± 50% VARIATION
IN INSTALLED COST OF CONVERTER

	BASE CASE (1)	+ 50%	-50%
DIRECT MANUFACTURING COST	5.14¢/lb.	5.14¢/lb.	5.14¢/lb.
INDIRECT MANUFACTURING COST	0.34	0.34	0.34
FIXED MANUFACTURING COSTS			
Depreciation - 10 year str. line	0.51	0.52	0.50
Insurance & Property Tax	0.12	0.12	0.12
MANUFACTURING COST	6.11¢/lb.	6.12¢/lb.	6.10¢/lb.
GENERAL EXPENSES			
Administration	0.18	0.18	0.18
Sales	0.06	0.06	0.06
Research	0.12	0.12	0.12
Finance	0.31	0.32	0.30
TOTAL MANUFACTURING COST, ¢/LB.	6.78	6.80	6.76
PRODUCT VALUE			
EtO @ 7.5¢/lb.	←	$15,000,000	→
Profit Before Taxes, $/yr.	1,440,000	1,400,000	$1,480,000
NPAT (52%) $/Yr.	691,200	672,000	710,400
ROI	6.8%	6.5%	7.1%

(1) CF Table EO-14.

TABLE EO-15
ETHYLENE OXIDE MANUFACTURING COST*
FOR NEW PLANT WITH STEAM GENERATION
200 MM LBS./YEAR FACILITY

OXYGEN OXIDATION PROCESS

DIRECT MANUFACTURING COST	¢/LB.	$/YR.
Raw Materials		
Ethylene	3.8	
Oxygen	1.0	
Catalyst & Chemicals	0.2	
Labor	0.31	
Maintenance	0.13	
Utilities	0.61	
	6.05	
INDIRECT MANUFACTURING COST		
Plant Overhead @ 110% of Labor	0.34	
FIXED MANUFACTURING COST		
Depreciation - 10 Yr. Straight Line	0.262	524,000
Insurance & Property Tax (2.3% of Inv.)	0.06	
	0.322	
MANUFACTURING COST	6.712	
GENERAL EXPENSES		
Administration (3% of Mfg. Cost)	0.20	
Sales (1% of Mfg. Cost)	0.07	
Research (2% of Mfg. Cost)	0.13	
Finance (6% of Investment)	0.16	
TOTAL COST	7.272	14,540,000
PRODUCT VALUE		
Ethylene Oxide @ 7.5¢/lb.		15,000,000
Profit Before Taxes		460,000
NPAT (52%)		220,800
Cash Flow		744,800
ROI	4.2%	

*Cost of steam generator taken from APCI (Catalytic, Inc.) file data. Other costs from Table EO-13. 1973 dollars.

TABLE EO-16
PRO-FORMA BALANCE SHEET
200 MM LBS./YR. ETHYLENE OXIDE MANUFACTURING FACILITY

	AIR OXIDATION PROCESS		OXYGEN OXIDATION PROCESS	
	EXISTING	MOST FEASIBLE NEW	EXISTING	MOST FEASIBLE NEW
Current Assets				
Cash (a)	1,018,333	1,018,333	1,116,667	1,118,667
Accounts Receivable (b)	1,250,000	1,250,000	1,250,000	1,250,000
Inventories (c)	1,354,000	1,356,000	1,450,000	1,454,400
Fixed Assets				
Plant	10,000,000	10,225,000	5,2000,000	5,240,000
Building	100,000	100,000	100,000	100,000
Land	50,000	50,000	50,000	50,000
	$13,772,333	$13,999,333	$9,166,667	$9,213,067
Current Liabilities (d)	976,666	973,333	1,130,000	1,131,667
Equity & Long Term Debt	12,795,667	13,026,000	8,036,667	8,081,400
Total Capital	$13,772,333	$13,999,333	$9,166,667	$9,213,067

(a) Based on one months total manufacturing cost.
(b) Based on one months sales.
(c) Based on 20 MM lbs. of product valued at total cost.
(d) Based on one months total cost less fixed manufacturing and finance costs.

XII. Cost to Industry

Current emission control devices on ethylene oxide plants are not very plentiful. This is due to two main factors. First, ethylene oxide is recovered in dilute form from the reactor effluent stream. All plants use a water absorber for this stream. Strictly speaking, these absorbers are not pollution control devices but necessary process equipment. Moreover, they do virtually nothing to remove hydrocarbons from the vent stream.

Secondly, the scrubbed gases from the main reaction section and the waste CO_2 purge gases are normally vented directly. All of these streams contain a few percent hydrocarbons and many of them are non-combustible and present a problem in cleaning up before releasing. The most feasible solution, employed by two respondents and mentioned as a desired improvement by others is a catalytic converter to burn these streams to CO_2 and H_2O and recover power from the hot gas. Cost of this equipment is roughly estimated at two percent of plant investment.

One respondent, whose process is unique, has a main process vent stream that is combustible. This stream is burned in a steam generator presumably off-site from the ethylene oxide unit. Unfortunately, there are no data available for this operation.

In the most feasible new plants shown in Tables EO-14 and 15, air pollution control equipment represents about one to two percent of plant investment. The resulting total production cost for ethylene oxide for these units would be about 0.01¢ per lb. higher using two air oxidation plants as comparison and about 0.02¢ using two oxygen oxidation plants as comparison.

Assuming all new plants built between now and 1985 incorporate these types of control equipment, the total incremental capital cost will be about $2,650,000 (1973 dollars), if the ratio of air to oxygen processes remains as it is today (i.e., 25 percent oxygen process).

The projected effect of this expenditure on future air emissions is shown on Table EO-17.

TABLE EO-17
ESTIMATED 1985 AIR EMISSIONS
FOR
ALTERNATIVE CONTROL SYSTEMS

Type of Pollution Control	Present Systems (1)			Present Systems (1)			Existing Plants Modified & New Plants Incorporating Most Feasible Control (3)		
Ethylene Oxide Production, MM Lbs./Year	4,191			6,800 (2)			6,800 (2)		
Pollutant	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted (4) Emissions MM Lbs./Yr.	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted (4) Emissions MM Lbs./Yr.	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted (4) Emissions MM Lbs./Yr.
Hydrocarbons	0.02048	85.83	6,866	0.02048	139.26	11,141	0.0049	33.32	2,666
Particulates	0.000007	0.03	2	0.000007	0.05	3	0.000007	0.05	3
NOx	0.000066	0.28	11	0.000066	0.45	18	0.0001	0.68	27
SOx	0.000031	0.13	3	0.000031	0.21	4	0.000031	0.21	4
CO	0.0	0	0	0.0	0	0	0.0	0	0
	0.02058	86.27	6,882	0.02058	139.97	11,166	0.00504	34.26	2,700

(1) Assumes questionnaires received are typical of industry, and without controls, growth will have identical emissions factors.

(2) Estimated total production by 1985. Assumes growth in same proportions as present, i.e., 66 percent air oxidation and Shell process for 86 percent of balance.

(3) Catalytic conversion of main process vents plus carbon dioxide vent on all air oxidation plants and incineration of main process vent on all oxygen oxidation plants.

(4) Weighting Factors: Hydrocarbons - 80, Particulates - 60, NOx - 40, SOx - 20, and CO - 1.

XIII. Emission Control Deficiencies

Technical deficiencies preventing reduced levels of emission include the following:

A. Process Chemistry and Kinetics

The direct oxidation of ethylene to ethylene oxide is a specific reaction promoted by a silver catalyst and one which must be carefully controlled in order to form ethylene oxide and not CO_2.

1. Reactor Feed

(a) Ethylene - any appreciable quantities of impurities could react with oxygen in the feed to form small quantities of oxygenated compounds in the reactor effluent, probably to the detriment of ethylene oxide formation and unnecessarily complicating the recovery and refining steps used to make 99+% pure ethylene oxide. Furthermore, some impurities compete with ethylene for the active catalyst sites and thus act as temporary poisons.

(b) Oxygen - either air or oxygen are satisfactory feed to the process. Of course, the plant must be designed for that particular feedstock. One patent claims that the amount of argon brought in with the oxygen influences catalyst activity.

2. Reactor Operating Conditions

This reaction is very sensitive to temperature. (See Section II) In order to maximize ethylene oxide yield and supress CO_2 formation, it is very important that the catalyst surface remain at the desired temperature and that there be no "hot spots". Since no one has designed the perfect isothermal reactor yet, there is bound to be some temperature gradient leading to formation of CO_2 as a by-product. Fortunately, CO_2 is not an air pollutant but unfortunately it results in a more dilute stream from which to remove pollutants. It also represents a dollar loss of ethylene which could have gone to ethylene oxide.

3. Catalyst

Considerable research has been done on producing a superior catalyst for ethylene oxide production. No metal yet tested can compete with the conversion/selectivity relationship of silver. Other important factors are use of a promotor and stabilizer for the catalyst (alkali and alkaline earth metals), the chemical nature and physical state of the support and the use of an oxidation deactivator such as ethylene dichloride.

B. Process Equipment and Operations

1. Reactors

The reaction producing ethylene oxide is exothermic but must be

carefully controlled to avoid going too far and producing CO_2 instead. As mentioned earilier, good heat transfer from the catalyst to the heat transfer medium is essential to maintain a controlled reaction. Optimum heat control could possibly be realized by using a fluidized bed instead of the universal fixed bed reactor with tubes used in all ethylene oxide plants. A fluid bed process was pilot planted but never commercialized. Apparently if one can attain good to excellent temperature control in a fixed bed (and many people do) ethylene oxide yields are higher and there is less of a problem with catalyst costs, activity, attrition, life and recovery. To hold emissions to a minimum, it is imperative that the reactors be operated to produce ethylene oxide maximum and not to leave large quantities of ethylene or hydrocarbons in the vent gas. Fortunately, it makes good economic sense to operate in this manner.

2. Absorbers

Since the concentration of ethylene oxide in the absorber feed is relatively low, care must be taken to insure proper operation of the absorber so as not to lose ethylene oxide product. Absorber operation was covered in Section X - Plant Inspection Procedures.

C. Control Equipment and Operations

The best method of reducing air emissions from air feed ethylene oxide plants is catalytic incineration of the two main vent streams. If the catalytic converter is operating properly, there are no SOx and CO emissions and little or no hydrocarbons and NOx. The only appreciable emissions should be CO_2, water, nitrogen and oxygen. Hence, this system really has no deficiencies in terms of emissions.

For an oxygen feed ethylene oxide plant, a steam boiler can be used to incinerate the main process vent gas since it is usually combustible. Again proper operation of the boiler firing should give only CO_2, H_2O, N_2, O_2, and perhaps traces of NOx in the exhaust gas. If there is no use for the steam produced, a thermal incinerator would be just as effective and cheaper to install but would not give any steam credit to the operation.

XIV. Research and Development Needs

The following programs are suggested as a way to improve ethylene oxide yield and simultaneously reduce air emissions.

A. Existing Plants

1. CO_2 Inhibitor

Presently some plants use PPM of chlorinated hydrocarbons (e.g., ethylene dichloride) as inhibitors for the reaction ethylene + O_2 $\longrightarrow$ CO_2. Obviously, if a better suppressant could be found, the yield of ethylene oxide from ethylene would improve. This change would probably not have a great positive effect in reducing air emissions as CO_2 is not considered a pollutant and unreacted ethylene would still be vented. However, it is a step in the right direction since reduction in CO_2 formation would require less venting of the recycle gas to the atmosphere.

2. Improved Catalyst

Development of a more selective catalyst to produce ethylene oxide from ethylene at the expense of CO_2 formation would have a double barreled value. First, more valuable product would be available to the producer and less by-product of little or zero value. Second, more efficient use of ethylene would result in more ethylene oxide and less unreacted ethylene to recycle and eventually vent as an air emission.

According to the literature, the choice of metal has been rather well worked over. Silver has been the best choice of all metals tested since the beginning of the air oxidation process. Although this ground has been ploughed thoroughly, it would bear checking again. Petroleum reforming catalyst has used platinum as the best choice since the inception of the process in the late 1940s. However, after 20 years of research on the catalyst, recent developments have lead to several bimetallic catalysts of far superior properties than the original platinum catalyst even though platinum is still the major ingredient. After 20 years of research on ethylene oxide catalyst, there is still the chance that the silver based catalyst could be improved or supplemented by another metal or metals.

Many more catalyst supports are available today than when the ethylene oxide silver catalyst was first developed. Surely not all of these have been tested. The proper choice of support for a given catalyst can mean the difference between a dead, a mediocre and an outstanding catalyst. This should be investigated.

Finally, the method of preparation of a given catalyst on its support can also mean the difference between a winner, a loser and an also ran. This field bears investigation, too.

3. Catalytic Incinerator

This type of device appears to be the best for reducing air emissions from ethylene oxide plants that utilize air oxidation, hence

the following factors should be considered:

(a) Complete combustion to CO_2 and H_2O should be sought. A two stage converter is a possible technique.

(b) The design should be optimized to give good performance at low installed cost. Some of these devices are very expensive.

(c) Units which fit existing plants with no incinerator present would be of value.

4. Steam Generator

In an oxygen oxidation plant, the main process vent is small compared to the CO_2 vent stream. It is normally rich enough to sustain combustion and can best be handled in a steam generator or a thermal incinerator. The stream is too small for feeding to a catalytic incinerator and using the hot gases as a power source to drive the feed turbines. But a steam generator will at least recover some energy for the user. Here, some work could be done to determine exactly which type of steam generator would be the most economical to install in this particular application.

Design work on a catalytic incinerator for air oxidation plants or a steam generator for an oxygen oxidation plant could best be performed by the manufacturers of these lines of equipment, or process licensors.

B. New Plants

In addition to the above R & D projects which could be used in either new or existing plants, the following would require new facilities and would not be totally applicable to existing plants.

1. Fluid Reactor

This process has already been piloted in the early 1950s but was never commercialized. In view of the giant strides taken in fluid catalyst technology in the past 20 years, it would be well to reinvestigate this process using either air or oxygen feed to see if it could be improved. The ultimate aim would be, as with an improved catalyst, to give a more selective process yielding more ethylene oxide, less CO_2 and consuming more of the ethylene which now goes out the vents as air emissions.

2. Fluid Catalyst

The success or failure of (1) above probably would hinge on development of a selective, attrition resistant and economical fluid catalyst (which was a problem when the fluid process was first investigated). One can not have one without the other.

C. Industry Background

It should be remphasized that most, if not all of the ideas covered in Sections A & B have been investigated by industry in the past. This is especially true in the field of catalyst research and development of the fluid process where much work has been done. It

is not to suggest that not enough has been done in these areas but rather to point out that here are two areas which can never be dismissed out of hand as long as new materials and techniques are being developed. For example, a new catalyst support which becomes commercially available might yield a breakthrough in preparing a high activity, high selectivity ethylene oxide catalyst from a metal or metals which had been tried before.

XV. Research and Development Programs

The following proposed projects relate to those areas of R & D which seem to offer the best change of obtaining a method of reducing emissions from ethylene oxide plants. They are both of the nature that requires considerable proprietary knowledge of catalyst so might best be conducted by licensors or suppliers of ethylene oxide processes and catalysts.

A. Project A

1. Title - Catalyst Modification Program

2. Objective: To make a preliminary screening study of variations on existing commercial ethylene oxide catalyst to see if any new leads could be uncovered to show the way to a better catalyst with respect to aging, selectivity or activity. This study would define the catalyst problem, but not necessarily solve it. It could open the door to a full scale catalyst investigation far beyond the content of this program.

3. Estimate Projects Costs (See Table EO-18 for Cost Breakdown)

Capital Expenditure	$ 25,700
Operating Costs	
Unit Operations	71,600
Services	30,300
Miscellaneous	4,500
Contingency	61,000
Total	193,100

4. Scope: This project would seek leads toward producing a better ethylene oxide catalyst which could improve yields and reduce plant emissions.

5. Program: A catalyst screening unit should be constructed with facilities for the calculation of the effluent by chromatographic procedures with emphasis on the quantitative analysis of by-products. The normal operating characteristics of the screening unit would be determined by employing a commercial supported silver catalyst. Experimental catalysts (perhaps) various noble metal alloys of silver and combinations of alkali oxide or alkaline earth metal promoters should be screened to determine if by-product formation can be reduced without adversely altering the main catalytic function. Investigation of various support media should also be carried out.

6. Timetable - It is estimated that the above program would require a total of 14 months to complete.

TABLE EO-18
DETAILED COSTS
FOR
R & D PROJECTS

	Project "A"	Project "B"
A. Capital Expenditures		
Test Unit Construction	$ 20,000	$ 20,000*
Unit Checkout		
Professional	3,600 (4 weeks)	3,600 (4 weeks)
Operator	2,100 (4 weeks)	2,100 (4 weeks)
B. Operating Expenses		
Unit Operation		
Professional	45,600 (50 weeks)	18,200 (20 weeks)
Operator	26,000 (50 weeks)	10,400 (20 weeks)
Services		
Analytical	3,300 (5 weeks)	2,000 (3 weeks)
Cat. Prep. & Testing	22,500 (45 weeks)	
Unit Maintenance	4,500 (10 weeks)	1,800 (4 weeks)
C. Miscellaneous		
Materials	3,000	1,000
Report Writing	1,500	1,500
D. Total of A to D	132,100	60,600
Contingency	61,100	30,300
	$193,100	$90,900

*NOTE: The test units for both projects will be quite similar. Should the projects be run sequentially, a single test unit would suffice, with appropriate savings.

B. Project B

1. Title - Improved CO_2 Inhibitor Program.

2. Objective: To begin a preliminary screening study of potential fuel additives which would inhibit the formation of CO_2 during the oxidation of ethylene. The project would hope to sort out several promising inhibitors but would not try to optimize them or devise new inhibitors. The results of this study could be used for these purposes.

3. Estimated Project Costs (See Table EO-18 for Cost Breakdown)

Capital Expenditures	$ 25,700
Operating Costs	
Unit Operations	28,600
Services	3,800
Miscellaneous	2,500
Contingency	30,300
	$ 90,900

4. Scope: This project would seek improved CO_2 formation inhibitors for the ethylene oxide process.

5. Program: A CO_2 formation inhibitor screening unit would be constructed with facilities for the evaluation of reaction products by chromatographic procedures, with emphasis on the quantitative analysis of CO_2. The normal operating characteristics of the screening unit should be determined by employing a standard organic halide inhibitor. Experimental inhibitors would be screened to determine if CO_2 formation can be reduced without adversely altering the activity/selectivity functions of the catalyst.

6. Timetable: It is estimated that the above program would require a total of ten months to complete.

XVI. Sampling, Monitoring and Analytical Methods for the Ethylene Oxide Process

This process is a fairly simple process to monitor. Stream components consist of CO_2, ethylene, ethylene oxide, oxygen, nitrogen, water vapor and traces of methane, ethane and other hydrocarbons. These are easily measured by conventional "on stream" analytical techniques. Typical analyses that can be performed are:

1. Ethylene measurement in the reactor feed gas for safety purposes to insure that the ethylene concentration is below the LEL. In the reactor effluent, the ethylene concentration is an indication of reaction efficiency. Ethylene is also measured in the recycle gas for build up.

2. Carbon dioxide is measured before and after the reactor indicating the amount of inerts in the stream as well as indirectly monitoring the reactor efficiency and possible combustion of ethylene to CO_2.

3. Ethylene oxide is monitored as a reactor product and in the recycle stream for checking product removal in the absorption system.

4. Oxygen is measured to insure sufficient oxygen to maintain the reaction, and for safety purposes.

5. Water vapor, nitrogen, argon and hydrocarbons can be measured for material balances.

6. Carbon monoxide can be measured if present in the recycle stream for indication of possible catalyst poisoning or side reactions.

When a complete analysis of the gas stream is required, gas chromatography is usually the method selected for measuring N_2, O_2, A, EtO, ethylene, etc. However, when continuous analysis of a single component in a multi-component stream is desired, oxygen can be analyzed by paramagnetic methods and non-dispersive infra red analysis can be used to measure CO, CO_2, ethylene, ethylene oxide, etc.

As is typical of many other types of chemical process industry, the survey revealed that monitoring of the various process streams is much more common than monitoring of emissions into the atmosphere. However, the analytical technology is quite similar and it may thus be presumed that most individual plants are capable of measurement of emissions without extensive investment in time or equipment. A summary of the information obtained concerning the methods in use is shown in Table EO-19.

In reviewing the information available on analytical techniques, it is apparent that multiple column gas chromatography is the method of choice in the industry. The specific methodology, however, is variable. From the air pollution standpoint, ethylene and ethylene oxide are or primary concern and can be separated on a two-column instrument. Prior to the adoption of any requirements for continuous or periodic monitoring of stack gases, it would appear advisable for the USEPA to develop a reference procedure for ethylene and ethylene oxide analysis. Such a project would involve an independent verification of the accuracy and specificity on one or more of the methods described in Table EO-19 and should be minor in scope.

TABLE EO-19
SUMMARY OF EMISSIONS MEASUREMENT TECHNIQUES
USED IN ETHYLENE OXIDE PLANTS

Plant Number	Source & Flow Rate	Sampling and Analytical Methods
13-1	Absorber Vent (24,000 SCFM)	Routine measurement of ethylene by extracting sample into a cylinder for laboratory analysis by infrared. Instrument and analytical details unknown. Occassional gas-liquid chromatography and mass spectrometer analysis of other constituents. Flow continuously metered.
	Stripper Vent (164 SCFM)	Samples collected once per year for laboratory analysis by GLC and Mass Spectrometer. Details unknown.
13-2	Compressor Vent (131,000 Lbs./Hr.)	Composition of the gas stream is continuous monitored by a combustion of chromatographs as described below. Flow is continuously metered. (1) Varian Model 1720, dual column, thermal conductivity. a. Column 1. Analysis for CO_2, C_2H_4, C_2H_6, A & O_2, N_2, and CH_4 on a Porepak R, 80-100 mesh column (7' x ¼" S.S) followed by 5A, 60-80 mesh molecular sieve (7' x ¼" S.S). The column is operated at ambient temperature. b. Column 2. Argon and oxygen are separated on 20' of ¼" S.S. containing 60-80 mesh, 5A molecular sieve at -25° C. (2) Varian Model 1740, single column flame ionization. Ethylene oxide is partitioned on a 7' x ¼" S.S. column containing 80-100 mesh, Porepak R, at 170° C.
	Reabsorber Vent (3,671 Lbs./Hr.)	The concentration of CH_4, C_2H_4, C_2H_6 and unidentified aldehydes is measured using a Varian Model 2740 chromatograph with flame ionization detector. The 7' x ¼" S.S. column contains 80-100 mesh Porepak R and is heated from 50° to 220° C at a rate of 10°/min. Samples are collected in a stainless cylinder. Stack flow is continuous metered.

TABLE EO-19
SUMMARY OF EMISSIONS MEASUREMENT TECHNIQUES
USED IN ETHYLENE OXIDE PLANTS

Plant Number	Source & Flow Rate	Sampling and Analytical Methods
13-3	Reabsorber Vent (200 SCFM)	Samples collected twice daily in a 500 CC stainless steel cylinder. Laboratory analysis by multiple-column and single column gas chromatography. Ethylene, carbon dioxide, oxygen and argon, and nitrogen are determined using a Fisher dual-column gas partitioner. Column one (¼" x 10') contains 30% HMPA on 60-80 mesh Chromosorb P and is used to measure ethylene and CO_2. The second column partitions oxygen and argon and nitrogen on 30-42 mesh, 13x molecular sieve (¼" x 5') followed by 5' of uncoated Chromosorb P. Ethylene oxide is measured on a Hewlett-Packard Model 700 with single column of 20% carbowax 20M on 60-80 mesh gas pack F (¼" x 10').
13-4	Process Vent (950 SCFM)	Samples are analyzed for ethylene on rare occasions by grab bag collection for laboratory gas chromatographic analysis.
13-5	Turbine Vent (16,550 SCFM)	One or two samples per month are collected in a glass bulb for analysis of ethylene by vapor-phase chromatography. Flow is continuously metered by an orifice.
	Absorber Vent (5,500 Lbs./Hr.)	One sample per month is collected in a stainless steel bomb for analysis as above. Flow is metered by orifice.
	Recovery Vent (480 SCFM)	The gas stream is piped to the laboratory for continuous analysis of ethylene oxide by vapor-phase chromatography. In addition, one to two samples per month are collected in a stainless bomb for ethylene analysis by GLC. Flow is monitored by orifice.
13-6	Cycle Gas Exhaust (64,000 SCFM)	Samples continuously pumped to laboratory through a sample line for ethylene oxide and ethylene analysis by Bandix gas chromatograph. Three columns are used, but their function is unknown. Column No. 1 contains 20% of 2-pentrile A on

TABLE EO-19
SUMMARY OF EMISSIONS MEASUREMENT TECHNIQUES
USED IN ETHYLENE OXIDE PLANTS

Plant Number	Source & Flow Rate	Sampling and Analytical Methods
13-6 (continued)	Cycle Gas Exhaust (64,000 SCFM)	30-60 mesh chromosorb; No. 2 contains grade 15 silica gel; and No. 3 is a 5A molecular sieve. Occasional analyses by Orsat and by $MgCl_2$ for ethylene and ethylene oxide are also run.
	Mixed Gas Exhaust	Occasional Orsat for gas composition.
13-7	Absorber Vent	Gas stream piped to gas chromatograph for hourly analysis. Details unknown Particulate measurements have been made using in-stack alundum thimble.
	Recovery Vent (1,050 SCFM)	Three analyses per year have been made for ethylene oxide using a mass spectrometer. Samples are collected in a bomb.

XVII. Emergency Action Plant for Air Pollution Episodes

A. Types of Episodes

The alleviation of Air Pollution Episodes as suggested by the U.S. Environmental Protection Agency is based on a pre-planned emission reduction scheme. The criteria that set this scheme into motion are:

1. Alert Status - The alert level is that concentration of pollutants at which short-term health effects can be expected to occur.

2. Warning Status - The warning level indicates that air quality is continuing to deteriorate and that additional abatement actions are necessary.

3. Emergency Status - The emergency level is that level at which a substantial endangerment to human health can be expected. These criteria are absolute in the sense that they represent a level of pollution that must not be allowed to occur.

B. Sources of Emission

As outlined in the foregoing in-depth study of ethylene oxide manufacture by the direct oxidation of ethylene, there are three continuous and some intermittent emissions occasioned by flaring or venting gas during plant upsets.

1. Continuous Streams

   (a) Main Process Vent Gas - This stream constitutes the greatest potential for air pollution. In the case of the air oxidation scheme it is emitted from the secondary or purge absorber. In the processing scheme using pure oxygen, the main process vent stream is from the CO_2 absorber. The composition and quantity of the main vent streams vary significantly between the two processing schemes that are used.

   These streams are handled in different ways depending on the processing scheme employed. In the air oxidation route the stream, in some instances, is diverted to a catalytic converter where hydrocarbons are converted to the products of combustion. The entire stream at elevated temperature is then used to drive a hot gas turbine before exhausting to the atmosphere. In the processing scheme using pure oxygen at least one operator adds methane to the recycle. This acts as an "inert" at the conditions of the process reactor but results in a vent gas that is suitable as boiler fuel.

   (b) Carbon Dioxide Rich Purge Gas - This stream, in the case of the air oxidation scheme, is emitted overhead of the ethylene oxide rectification or lights removal column. Its composition is essentially N_2, O_2, CO_2 and water with

some ethylene. The comparable stream in the oxygen scheme of processing is emitted from the overhead of the regenerator or stripper of the CO_2 absorption system. This system is to reduce CO_2 concentration in the recycle gas. The composition of the stream is essentially CO_2 and water with some ethane and ethylene present. These streams are relatively small in volume with the most voluminous emission from the oxygen mode of processing. These streams are normally vented directly to the atmosphere. In some plants the CO_2 purge stream is scrubbed to recover ethylene oxide.

(c) Turbine Exhaust - The emission from this source is the result of using hot gas turbines to drive the air compressor and charge ethylene to the process. The turbines are powered with natural gas and, since their efficiency is something less than 100 percent, the stream emitting to the atmosphere can be a significant contributor to the emission of hydrocarbon pollutants. A fired gas turbine is used on at least one air oxidation facility and should not be mistaken for the hot gas turbine mentioned earlier. In the latter instance, on at least two air oxidation facilities, the main process vent stream passes through a catalytic converter with its effluent, at elevated temperature, driving the gas turbine.

2. Intermittent Air Emissions

(a) As in any process there are instances in the operation whereby flaring or venting of process streams occur during upset conditions for safety purposes or during shutdowns when equipment is prepared for entering. In general these are short periods with insignificant emissions on a yearly basis. In most instances of shutdown venting, the emissions could be curtailed if it should occur during an air pollution episode. An exception to this regulation would be the venting and safing of the reactors if it is deemed necessary to prevent damage to the catalyst.

C. Abatement Techniques

As the various levels of the pre-planned episode reduction scheme are declared (Alert, Warning and Emergency) a progressive reduction in the amount of air pollutants must be made. This could ultimately lead to total curtailment of pollutant emissions if the emergency level becomes imminent.

Although these instructions for the "Air Pollution Episode Avoidance Plan" are designed for ethylene oxide manufacturing plants, the overall Emergency Action Plan (EAP) will cover all aspects of environmental air pollution. Consequently, the implementation of the pre-planned episode reduction scheme, as it applies to ethylene oxide manufacture, will be in consideration of reductions made in all sources of air pollutants as well as to the specific offending constitutents in the atmosphere. Therefore, the extent of required cutback in emissions from ethylene oxide plants will depend on the relative amounts of air pollutants contributed by ethylene oxide production to the overall emissions which resulted in the pollution episode. These factors will be used by the Governing Environmental Protection Authority in determining the cutback to be made in all air pollution sources during the various episodes.

Ethylene oxide manufacturing facilities by the direct oxidation of ethylene consist of a bank of primary reactors, which are operated in parallel, a primary absorber, a secondary (purge) ethylene conversion system and a purification system for the removal of CO_2 and inert gases and heavy ends. In the oxygen mode of operation the secondary system is comprised of a CO_2 absorber and regenerator for control of the CO_2 in the recycle gas stream. Although there are significant differences in the design of the plants employing air oxidation versus the use of oxygen, with respect to the recovery sections, the control of emissions during air pollution episodes would be handled in essentially the same manner.

Based upon information obtained from several plants, it appears that a reduction in operating rate results in reductions in emissions from the purge absorber vent in air based plants. One respondent reported a reduction in hydrocarbon emissions of 75 percent by a reduction in production rate of 1/3 with further decreases in emissions by reducing the production rate to the minimum operating level (50 percent of design. However, it is felt that only minimum advantages would accrue on those plants equipped with catalytic converters. Other respondents also report a decrease in emissions with a turndown in production but with a significantly smaller decrease in emissions. This also applies to the CO_2 purge vent on the plants that use oxygen to accomplish the oxidation of ethylene. It was also reported that a small reduction in hydrocarbon emissions from the CO_2 purge stream was possible by change in operating conditions. The flow from the ethylene oxide rectification or lights removal column is reported as being proportional to production rate. Consequently, a turndown in capacity could accomplish a partial reduction in emissions during an air pollution episode. Under normal conditions a turndown to a predetermined rate can be accomplished with a 24 hour period. It is visualized that during this period there would be a progressive decrease in emissions. Another method to obtain a partial decrease in emissions would be a shutdown of one or more reactors. It is indicated, however, in one of the E.O. processes that the decrease in emission would not be proportional to the number of reactors taken out of service. Matter of fact, it was stated that a shutdown of one or more primary reactors has very little effect on the emission of pollutants. Moreover, it may increase the emissivity for a short period if it is deemed necessary to vent and safe the reactors in order to protect the catalyst. Start-up of a reactor taken out of service would depend on conditions maintained during the shutdown. Eight to 16 hours would be required to resume operation.

It should be noted that the oxidation of ethylene is an exothermic reaction with the exotherm consumed within the process to generate steam. Any reduction in plant capacity could result in a steam deficient condition within the confines of the E.O plant itself and possibly over greater areas of a complex. Consequently, the steam load within the central boiler plant would probably increase with the attendant increase in emissions from this source.

There are several items of equipment that can be classed as emission control devices among the reporting plants. Two respondents indicated the use of catalytic converters on the secondary or purge absorber vent. One respondent reported the use of a steam generator and two use vent gas scrubbers on the CO_2 purge stream while another reports the use of a flare stack for emergencies. In plants employing catalytic converters whose effluent is used to drive process turbines, a partial

reduction in plant capacity may adversely effect both the converter and turbine. In these instances it seems reasonable to assume that some standby source of power would be available as an alternative to drive the turbine. In the case where a steam generator is partially dependent on the combustibles contained in the vent stream, some adjustment would seem to be in order to maintain the rate of steam generation. In these instances, however, methane is normally injected to the lean hydrocarbon vent stream for the required flammability limit. In a partial reduction in plant capacity, the methane content of the gas mixture will increase if the methane injection rate is held constant. This results from less argon and nitrogen intake with lower oxygen use rate. Also, CO_2 generation rate will decrease, therefore, the gas mixture will be richer in methane. With respect to the vent gas scrubbers on the CO_2 purge stream, a reduction in total flow to the scrubber should improve the efficiency of this equipment over that obtained at normal ethylene oxide production levels.

1. Declaration of Alert Condition

When an alert condition in the atmosphere becomes apparent, the episode emission reduction plan is immediately set into motion. Under this plan the Environmental Protection Authorities declare that such a condition has developed and promptly notify the manufacturers to proceed with their alert preparations. Under this plan, depending on the rate at which the pollutant concentration is progressing, type of pollutant and the meteorology potential that exists at the time, it may be deemed necessary by the Environmental Protection Authorities to proceed with a partial reduction in emissions from ethylene oxide manufacture to prevent further increases in pollution level. This reduction would be accomplished by a reduction in plant production as previously discussed. The time required to affect the reduction will be approximately as stated in the foregoing. This will reduce the principal source of emission represented by the main process vent from the purge absorber and the CO_2 rich purge gas. In the case of the exhaust from the hot gas turbine powered by natural gas, a turndown of plant production would not necessarily reduce total hydrocarbon emissions from this source. Most gas driven turbines, however, are capable of some degree of turndown that may be used during a partial reduction in production. In this event a reduction in non-methane hydrocarbon emissions would be anticipated. In those facilities that employ a catalytic converter for the main process vent, a reduction in emissions may have an adverse effect. This in turn could present difficulties in the operation of the downstream gas turbine driver. In this event pollutant emissions may actually increase from this source if the utmost care is not exercised in the operations directed to a partial reduction in plant capacity.

2. Declaration of Warning Condition

If it becomes apparent that the efforts directed to the curtailment of air pollutants have not resulted in an improvement in air quality during the alert a warning condition is then declared. When the air pollution warning episode is announced a substantial reduction of air contaminants is desirable even to the point of assuming reasonable economic hardship in the cutback of production and allied operations. This could involve a 50-60 percent decrease in ethylene oxide production.

3. Emergency Condtion

When air quality has deteriorated to a point where it appears that an emergency episode is imminent, all air contaminants may have to be eliminated immediately by ceasing production and allied operations to the extent possible without causing injury to persons or damage to equipment.

D. Economic Considerations

The economic impact on ethylene oxide manufacturers of curtailing operations during any of the air pollution episodes is based on the duration and number of episodes in a given period. It is indicated that the usual duration of air pollution episodes is one to seven days with meteorology potentials as high as 80 per year.[15] The frequency of air pollution episodes in any given area is indicated as being one to four years. These data do not differentiate between the episode levels set forth in the early paragraphs of this section. Normally since the alert level does not require a cutback in production, it will not significantly influence plant economics. Therefore, in discussing economic considerations resulting from the air pollution abatement plan, it is only necessary to estimate the frequency and number of warning and emergency episodes. For the economic study, it has been assumed that three warning and no emergency episodes occur per year. Each warning episode is assumed to require a 50 percent reduction in air contaminants for a period of 5½ days. This equates to a complete loss in plant production of about 8½ days per year.

The financial impact resulting from this loss in production is shown in Table EO-20. This table presents comparative manufacturing costs of both the oxygen and air oxidation modes of operation in typical existing 200 MM lbs./year facilities without extensive pollution control and typical new plants of the same capacity. Economics are shown for each of these with and without the financial impact accredited to the air pollution episodes. It should be noted that whereas the proposed cutback in ethylene oxide production for emission control appears small (2.5 percent on a yearly basis), it reduced net income for the oxygen oxidation process' by 20 percent and for the air oxidation process by 10 percent.

E. Summary of Estimated Emissions

In the foregoing a reduction in plant production was suggested to obtain a reduced rate of air pollutant emissions for the various air pollution levels that may be encountered. This was primarily predicated on existing plants with no pollution control equipment. Therefore, less stringent requirements should be provided in the EAP for Air Pollution Episode Avoidance for existing plants that employ control devices which substantially reduce emissions. Also, for those existing plants that install such equipment and for future plants that are equipped with the "latest state of the art" emission control equipment.

Table EO-17 presents estimated 1985 air emissions for the present-day systems without control devices versus emissions projected for existing modified facilities and new plants incorporating the most feasible devices. The control devices assumed to be incorporated in the latter category are: catalytic conversion of main process vents plus carbon dioxide vent on all air oxidation plants and incineration of main process vent on all oxygen oxidation plants. Emissions from the modified and new plants have been estimated to be reduced substantially from the estimates for the existing uncontrolled facilities.

TABLE EO-20

FINANCIAL IMPACT OF AIR POLLUTION EPISODES

ON MANUFACTURING COSTS

FOR 200 MM LBS./YEAR ETHYLENE OXIDE MANUFACTURING FACILITIES

VIA DIRECT OXIDATION OF ETHYLENE

	OXYGEN OXIDATION PROCESS				AIR OXIDATION PROCESS			
	TYPICAL EXISTING PLANT		NEW PLANT WITH STEAM GENERATING		TYPICAL EXISTING PLANT		NEW PLANT WITH CAT. INCINERATION	
	From Table EO-13 No Cutback In Production	Assuming 8.5 Days Lost Production	From Table EO-15 No Cutback In Production	Assuming 8.5 Days Lost Production	From Table EO-13 No Cutback In Production	Assuming 8.5 Days Lost Production	From Table EO-14 No Cutback In Production	Assuming 8.5 Days Lost Production
Direct Manufacturing Cost, M $/Yr.								
Raw Materials								
Ethylene	7,600	7,410	7,600	7,410	7,600	7,410	7,600	7,410
Oxygen	2,000	1,950	2,000	1,950	0	0	0	0
Catalyst & Chemicals	400	390	400	390	400	390	400	390
Labor	620	620	620	620	620	620	620	620
Maintenance	260	260	260	260	500	500	510	510
Utilities	1,200	1,170	1,220	1,190	1,200	1,170	1,150	1,120
Indirect Manufacturing Cost, M $/Yr.								
Plant Overhead	680	680	680	680	680	680	680	680
Fixed Manufacturing Cost, M $/Yr.								
Depreciation, Insurance & Property Tax	640	640	640	640	1,220	1,220	1,260	1,260

TABLE EO-20

FINANCIAL IMPACT OF AIR POLLUTION EPISODES

ON MANUFACTURING COSTS

FOR 200 MM LBS./YEAR ETHYLENE OXIDE MANUFACTURING FACILITIES

VIA DIRECT OXIDATION OF ETHYLENE

PAGE 2 - CONTINUED

	OXYGEN OXIDATION PROCESS				AIR OXIDATION PROCESS			
	TYPICAL EXISTING PLANT		NEW PLANT WITH STEAM GENERATING		TYPICAL EXISTING PLANT		NEW PLANT WITH CAT. INCINERATION	
	From Table EO-13 No Cutback In Production	Assuming 8.5 Days Lost Production	From Table EO-15 No Cutback In Production	Assuming 8.5 Days Lost Production	From Table EO-13 No Cutback In Production	Assuming 8.5 Days Lost Production	From Table EO-14 No Cutback In Production	Assuming 8.5 Days Lost Production
Manufacturing Cost, M $/Yr.	13,400	13,120	13,420	13,140	12,220	11,990	12,220	11,990
General Expenses								
Administration, Sales, Research and Finance	1,100	1,100	1,120	1,120	1,320	1,320	1,340	1,340
Total Cost, M $/Yr.	14,500	14,220	14,540	14,260	13,540	13,310	13,560	13,330
Product Value								
Ethylene Oxide @ 7.5¢/Lb.	15,000	14,625	15,000	14,625	15,000	14,625	15,000	14,625
Profit Before Taxes	500	405	460	365	1,460	1,315	1,440	1,295
NPAT	240	194	220	175	701	631	691	622
Cash Flow	760	714	745	699	1,701	1,631	1,711	1,642
ROI	4.6%	3.7%	4.2%	3.3%	7.0%	6.3%	6.8%	6.1%

The particular type and concentration of pollutants in the atmosphere at the time of the episode would dictate the degree to which a reduction would be made on the existing modified plant or the new facility. If the offending pollutants are in the form of hydrocarbons, the degree of cut-back on the modified or new plants could be proportionally less severe than on the uncontrolled facility. If NOx is the offending material, a reduction in plant production would reduce the amout of NOx being emitted from thermal incinerators or flares by virtue of reduced combustibles in their feed stream with attendant lowering of flame temperature. NOx production is a rate controlled phenomenon which is primarily controlled by flame temperature. Cooler flames and combustion zones tend to produce lower NOx concentrations. It is reported that substantially all of the NOx formed in a thermal device is formed in the high temperature region (2800° F) of the burner flame itself. At the temperature of the main residence-time section (1200-1500° F), the overall rate of reaction of nitrogen with oxygen is too slow for significant formation of NOx. It is for this reason that catalytic converters produce little if any NOx.

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APPENDIX I-1

BASIS OF THE STUDY

I. Industry Survey

The study which led to this document was undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study was to provide data for the EPA to use in the fulfillment of their obligations under the Clean Air Amendments of 1970.

The information obtained during the study includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an Industry Questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

More than 200 petrochemicals are currently produced in the United States, and many of these by two or more different processes. It was obvious that the most immediate need was to study the largest tonnage, fastest growth processes that produce the most pollution. Consequently, the following 32 chemicals (as produced by a total of 41 different processes) were selected for study:

Acetaldehyde (two processes)
Acetic Acid (three processes)
Acetic Anhydride
Acrylonitrile
Adipic Acid
Adiponitrile (two processes)
Carbon Black
Carbon Disulfide
Cyclohexanone
Ethylene
Ethylene Dichloride (two processes)
Ethylene Oxide (two processes)
Formaldehyde (two processes)
Glycerol
Hydrogen Cyanide
Maleic Anhydride
Nylon 6
Nylon 6,6
"Oxo" Alcohols and Aldehydes
Phenol
Phthalic Anhydride (two processes)
Polyethylene (high density)
Polyethylene (low density)
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene - Butadiene Rubber
Terephthalic Acid (1)
Toluene Di-isocyanate (2)
Vinyl Acetate (two processes)
Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

The Industry Questionnaire, which was used as the main source of information, was the result of cooperative efforts between the EPA, Air Products and the EPA's Industry Advisory Committee. After receiving approval from the Office of Management and Budget, the questionnaire was sent to selected producers of most of the chemicals listed above. The data obtained from the returned questionnaires formed the basis for what have been named "Survey Reports". These have been separately published in four volumes, numbered EPA-450/3-73-005a, b, c, and d and entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volumes I, II, III, and IV.

The purpose of the survey reports was to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix II of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emission Summary Table that constitutes part of this Appendix (Table I). This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs, and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were developed for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) were used.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR were used.

The bases for these ratings and example calculations are included in Appendix III of this report.

II. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furnace Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

TABLE I
EMISSIONS SUMMARY

	ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	66
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.04	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.5	8.6	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.8	0	0.14	30	1,190
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.8	1,870	2,060	77,364
Carbon Disulfide	0.15	0.3	0.1	4.5	0	5.1	179
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+IPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.4	0	0	21.8	117.3	7,850
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocyanates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo Process	5.25	0.01	0.07	0	19.3	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High Density Polyethylene	79	2.3	0	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	0	18.2	1,450
Totals	1,227.6	49.1	96.2	31.9	4,852.6	6,225.9 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Prob. Err has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE I
EMISSION SUMMARY

ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR

	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.06	0	0	0.06	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.3	14.5	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	86	3.1	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	6,040
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,750
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) See sheet 1 of 3.

TABLE 1
EMISSIONS SUMMARY

	Emissions (2), MM lbs./year		Estimated Number of New Plants (1971 - 1980)	Total Estimated Capacity MM lbs./year	
	Total by 1980	Total Weighted (3) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	4	1,160	2,400
via Ethanol	27	27	0	960	960
Acetic Acid via Methanol	0.05	1	4	400	1,800
via Butane	56	3,215	0	1,020	500
via Acetaldehyde	22	1,470	1	870	2,015
Acetic Anhydride via Acetic Acid	10.8	311	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,160	3,700 (8)
Adipic Acid	50	1,970	5	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	1	280	550
Carbon Black	5,730	24,760	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	861	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (→TPA)	265	13,300	8	2,867	5,900
Ethylene	94	3,670	21	22,295	40,080
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	13	4,195	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	60	3,915	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,120 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	458	10	1,088	2,120
Maleic Anhydride	500	5,670	6	359	720
Nylon 6	4.7	284	10	480	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,725	3,000
Phenol	46	3,640	11	2,363	4,700
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	7,315	8,500
Low Density Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	132	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	6	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,600	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probable bias up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons = 80, particulates = 80, NO_x = 40, SO_x = 20, and CO = 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut down of marginal plants.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional chemicals be "nominated" for in-depth study. These were phthalic anhydride, formaldehyde and ethylene oxide. Consequently, four additional in-depth studies were undertaken, as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.

2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst. (Also, the subject of a survey report.)

3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.

4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

The primary data source for these was the Industry Questionnaire, although SEI rankings had not been completed by the time the choices were made.

The Survey Reports, having now been completed are available, for use in the selection of additional processes for in-depth study.

INTRODUCTION TO APPENDIX II AND III

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix II discussion are:

1. Prediction of numbers of new plants.

2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix III discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX II-1

Number of New Plants*

Attached Table I illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

*The format is based on 1980, but any future year may be selected.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It was felt that no useful end is served by creating a large number of sub-groupings because it would merely compound the problem of assigning a weighting factor. Therefore, it was proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x. However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

	Babcock	Walther	
		Primary	Secondary
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it was proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	Average	Rounded
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical _____

Process _____

Increased Capacity _____

Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO_x			40	
SO_x			20	
CO			1	
			Total	

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.

2. Approximately two orders of magnitude exist between top and bottom rankings.

3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane are included.

4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.

5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.

6. NO_X should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. (This determination was made, on the basis of data reported on returned questionnaires, in the Survey Reports.

2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.

3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.

4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It was proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

(1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it was proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It was recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it was recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it was recommended that complete combustion be defined as the production of N_2, thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7\,O_2 \longrightarrow C + 2\,CO + 3\,CO_2 + 6\,H_2O$$

Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

Pollutant	Weighting Factor	Pounds in		Pounds out	
		Actual	Weighted	Actual	Weighted
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO_x	40	0		1	40
SO_x	20	0		0	
CO	1	0		66.5	66.5
Total			8000		958.5

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2\ CH_3Cl + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + 2\ HCl$$

This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

$$4\ HCN + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2 + 2\ N_2$$

$$N_2\ (\text{atmospheric}) + XO_2 \longrightarrow 2\ NO_x$$

Thus, $CCR_1 = 100\%$ and $CCR_2 = 100\%$ both by definition.

However, $SERR_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$

and $SERR_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it was suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 100 = 95\%$$

$$\text{and } SERR = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100$$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

$$\text{and } SERR = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$